EXHIBIT 1006
(CONTINUED)

A particulate scrubber may be considered as consisting of two parts: (1) a contactor stage, in which a spray is generated and the dust-laden gas stream is brought into contact with it; and (2) an entrainment separation stage, in which the spray and deposited dust particles are separated from the cleaned gas. These two stages may be separate or physically combined. The contactor stage may be of any form intended to bring about effective contacting of the gas and spray. The spray may be generated by the flow of the gas itself in contact with the liquid, by spray nozzles (pressure-atomizing or pneumatic-atomizing), by a motor-driven mechanical spray generator, or by a motor-driven rotor through which both gas and liquid pass.

Entrainment separation is accomplished with inertial separators, which are usually cyclones or impingement separators of various forms. If properly designed, these devices can remove virtually all droplets of the sizes produced in scrubbers. However, reentrainment of liquid can take place in poorly designed or overloaded separators.

Scrubber Types and Performance The diversity of particulate scrubber designs is so great as to defy any detailed and self-consistent system of classification based on configuration or principle of operation. However, it is convenient to characterize scrubbers loosely according to prominent constructional features, even though the modes of operation of different devices in a group may vary widely.

A relationship of power consumption to collection efficiency is characteristic of all particulate scrubbers. Attaining increased efficiency requires increased power consumption, and the power consumption required to attain a given efficiency increases as the particle size of the dust decreases. Experience generally indicates that the power consumption required to provide a specific efficiency on a given dust does not vary widely even with markedly different devices. The extent to which this generalization holds true has not been fully explored, but the known extent is sufficient to suggest that the underlying collection mechanism may be essentially the same in all types of particulate scrubbers.

Since some relationship of power consumption to performance appears to be a universal characteristic of particulate scrubbers, it is useful to characterize such devices broadly according to the source from which the energy is supplied to the gas-liquid contacting process. The energy may be drawn from (1) the gas stream itself, (2) the liquid stream, or (3) a motor driving a rotor. For convenience, devices in these classes may be termed respectively (1) gas-atomized spray scrubbers, (2) spray, or preformed-spray, scrubbers, and (3) mechanical scrubbers. In the spray scrubbers, all the energy may be supplied from the liquid, using a pressure nozzle, but some or all may be provided by compressed air or steam in a two-fluid nozzle or by a motor driving a spray generator.

Particulate scrubbers may also be classed broadly into low-energy and high-energy scrubbers. The distinction between the two classes is arbitrary, since the devices are not basically different and the same device may fall into either class depending on the amount of power it consumes. However, some differences in configuration are sometimes necessary to adapt a device for high-energy service. No specific level of power consumption is commonly agreed upon as the boundary between the two classes, but high-energy scrubbers may be regarded as those using sufficient power to give substantial efficiencies on submicrometer particles.

Scrubber Performance Models A number of investigators have made theoretical studies of the performance of venturi scrubbers and have sought to produce performance models, based on first principles, that can be used to design a unit for a given duty without recourse to experimental data other than the particle size and size distribution of the dust. Among these workers are Calvert [*Am. Inst. Chem. Eng. J.*, **16,** 392 (1970); *J. Air Pollut. Control Assoc.*, **24,** 929 (1974)], Boll [*Ind. Eng. Chem. Fundam.*, **12,** 40 (1973)], Goel and Hollands [*Atmos. Environ.*, **11,** 837 (1977)], and Yung et al. [*Environ. Sci. Technol.*, **12,** 456 (1978)]. Comparatively few efforts have been made to model the performance of scrubbers of types other than the venturi, but a number of such models are summarized by Yung and Calvert (U.S. EPA-600/8-78-005b, 1978).

The various venturi-scrubber models embody a variety of assumptions and approximations. The solutions of the equations for particulate collection must in general be determined numerically, although Calvert et al. [*J. Air Pollut. Control Assoc.*, **22,** 529 (1972)] obtained an explicit equation by making some simplifying assumptions and incorporating an empirical constant that must be evaluated experimentally; the constant may absorb some of the deficiencies in the model. Although other models avoid direct incorporation of empirical constants, use of empirical relationships is necessary to obtain specific estimates of scrubber collection efficiency. One of the areas of greatest uncertainty is the estimation of droplet size.

Most of the investigators have assumed the effective drop size of the spray to be the Sauter (surface-mean) diameter and have used the empirical equation of Nukiyama and Tanasawa [*Trans. Soc. Mech. Eng., Japan*, **5,** 63 (1939)] to estimate the Sauter diameter:

$$D_o = \frac{1920\sqrt{\sigma_L}}{V_o\sqrt{\rho_L/62.3}} + 75.4\left(\frac{\mu_L}{\sqrt{\sigma_L\rho_L/62.3}}\right)^{0.45}\left(\frac{1000Q_L}{Q_G}\right)^{1.5} \quad (17\text{-}3)$$

where D_o = drop diameter, μm; V_o = gas velocity, ft/s; σ_L = liquid surface tension, dyn/cm; ρ_L = liquid density, lb/ft^3; μ_L = liquid viscosity, cP; Q_L = liquid flow rate, ft^3/s; and Q_G = gas flow rate, ft^3/s.

The Nukiyama-Tanasawa equation, which is not dimensionally homogeneous, was derived from experiments with small, internal-mix pneumatic atomizing nozzles with concentric feed of air and liquid (Lapple et al., "Atomization: A Survey and Critique of the Literature," Stanford Res. Inst. Tech. Rep. No. 6, AD 821-314, 1967; Lapple, "Atomization," in *McGraw-Hill Encyclopedia of Science and Technology,* 5th ed., vol. 1, McGraw-Hill, New York, 1982, p. 858). The effect of nozzle size on the drop size is undefined. Even within the range of parameters for which the relationship was derived, the drop sizes reported by various investigators have varied by twofold to threefold from those predicted by the equation (Boll, op. cit.). The Nukiyama-Tanasawa equation has, nevertheless, been applied to large venturi and orifice scrubbers with configurations radically different from those of the atomizing nozzles for which the equation was originally developed.

Primarily because of the lack of adequate experimental techniques (particularly, the production of appropriate monodisperse aerosols), there has been no comprehensive experimental test of any of the venturi-scrubber models over wide ranges of design and operating variables. The models for other types of scrubbers appear to be essentially untested.

Contacting Power Correlation A scrubber design method that has achieved wide acceptance and use is based on correlation of the collection efficiency with the power dissipated in the gas-liquid contacting process, which is termed "contacting power." The method originated from an investigation by Lapple and Kamack [*Chem. Eng. Prog.*, **51,** 110 (1955)] and has been extended and refined in a series of papers by Semrau and coworkers [*Ind. Eng. Chem.*, **50,** 1615 (1958); *J. Air Pollut. Control Assoc.*, **10,** 200 (1960); **13,** 587 (1963); U.S. EPA-650/2-74-108, 1974; U.S. EPA-600/2-77-234, 1977; *Chem. Eng.*, **84**(20), 87 (1977); and "Performance of Particulate Scrubbers as Influenced by Gas-Liquid Contactor Design and by Dust Flocculation," EPA-600/9-82-005c, 1982, p. 43]. Other workers have made extensive independent studies of the correlation method [Walker and Hall, *J. Air Pollut. Control Assoc.*, **18,** 319 (1968)], and numerous studies of narrower scope have been made. The major conclusion from these studies is that the collection efficiency of a scrubber on a given dust is essentially dependent only on the contacting power and is affected to only a minor degree by the size or geometry of the scrubber or by the way in which the contacting power is applied. This contacting-power rule is strictly empirical, and the full extent of its validity has still not been explored. It has been best verified for the class of gas-atomized spray scrubbers, in which the contacting power is derived from the gas stream and takes the form of gas pressure drop. Tests of the equivalence of contacting power supplied from the liquid stream in pressure spray nozzles have been far less extensive and are strongly indicative but not yet conclusive. Evidence for the equivalence of contacting power from mechanically driven devices is also indicative but extremely limited in quantity.

Contacting power is defined as the power per unit of volumetric gas flow rate that is dissipated in gas-liquid contacting and is ultimately converted to heat. In the simplest case, in which all the energy is

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obtained from the gas stream in the form of pressure drop, the contacting power is equivalent to the friction loss across the wetted equipment, which is termed "effective friction loss," F_E. The pressure drop may reflect kinetic-energy changes rather than energy dissipation, and pressure drops that result solely from kinetic-energy changes in the gas stream do not correlate with performance. Likewise, any friction losses taking place across equipment that is operating dry do not contribute to gas-liquid contacting and do not correlate with performance. The gross power input to a scrubber includes losses in motors, drive shafts, fans, and pumps that obviously should be unrelated to scrubber performance.

The effective friction loss, or "gas-phase contacting power," is easily determined by direct measurements. However, the "liquid-phase contacting power," supplied from the stream of scrubbing liquid, and the "mechanical contacting power," supplied by a mechanically driven rotor, are not directly measurable; the theoretical power inputs can be estimated, but the portions of these quantities effectively converted to contacting power can only be inferred from comparison with gas-phase contacting power. Such data as are available indicate that the contributions of contacting power from different sources are directly additive in their relation to scrubber performance.

Contacting power is variously expressed in units of MJ/1000 m^3 (SI), kWh/1000 m^3 (meter-kilogram-second system), and hp/(1000 ft^3/min) (U.S. customary). Relationships for conversion to SI units are

$$1.0 \text{ kWh}/1000 \text{ m}^3 = 3.60 \text{ MJ}/1000 \text{ m}^3$$

$$1.0 \text{ hp}/(1000 \text{ ft}^3/\text{min}) = 1.58 \text{ MJ}/1000 \text{ m}^3$$

The gas-phase contacting power P_G may be calculated from the effective friction loss by the following relationships:

SI units:

$$P_G = 1.0F_E \tag{17-4}$$

where F_E = kPa.

U.S. customary units:

$$P_G = 0.1575F_E \tag{17-5}$$

where F_E = in of water.

The power input from a liquid stream injected with a hydraulic spray nozzle may usually be taken as approximately equal to the product of the nozzle feed pressure p_F and the volumetric liquid rate. The liquid-phase contacting power P_L may then be calculated from the following formulas:

SI units:

$$P_L = 1.0p_F(Q_L/Q_G) \tag{17-6}$$

where p_F = kPa gauge, and Q_L and Q_G = m^3/s.

U.S. customary units:

$$P_L = 0.583p_F(Q_L/Q_G) \tag{17-7}$$

where p_G = lbf/in^2 gauge, Q_L = gal/min, and Q_G = ft^3/min.

The correlation of efficiency data is based on the total contacting power P_T, which is the sum of P_G, P_L, and any power P_M that may be supplied mechanically by a power-driven rotor.

In general, the liquid-to-gas ratio does not have an influence independent of contacting power on the collection efficiency of scrubbers of the venturi type. This is true at least of operation with liquid-to-gas ratios above some critical lower value. However, several investigations [Semrau and Lunn, "Performance of Particulate Scrubbers as Influenced by Gas-Liquid Contactor Design and by Dust Flocculation," EPA-600/9-82-005c, 1982, p. 43; and Muir et al., *Filtr. Sep.*, **15,** 332 (1978)] have shown that at low liquid-to-gas ratios relatively poor efficiencies may be obtained at a given contacting power. Such regions of operation are obviously to be avoided.

It has sometimes been asserted that multiple gas-liquid contactors in series will give higher efficiencies at a given contacting power than will a single contacting stage. However, there is little experimental evidence to support this contention. Lapple and Kamack (op. cit.) obtained slightly higher efficiencies with a venturi and an orifice in series than they did with a venturi alone. Muir and Mihisei [*Atmos. Environ.*, **13,** 1187 (1979)] obtained somewhat higher efficiencies on two redispersed dusts when using two venturis in series rather than one. The improvement obtained with two-stage scrubbing was greatest with the coarser of the two dusts and was relatively small with the finer dust. Flocculation or deflocculation of the dusts may have been responsible for some of the behavior encountered. Semrau et al. (EPA-600/2-77-234, 1977) compared the performance of a four-stage multiple-orifice contactor with that of a single-orifice contactor, using well-dispersed aerosols generated from ammonium fluorescein, The multiple-orifice contactor gave about the same efficiency as the single-orifice in the upper range of contacting power but lower efficiencies in the lower range. The deviations in performance in this case were probably characteristic of the particular multiple-orifice contactor rather than of multistage contacting as such.

Most scrubbers actually incorporate more than one stage of gas-liquid contacting even though these may not be identical (e.g., the contactor and the entrainment separator). The preponderance of evidence indicates that multiple-stage contacting is not inherently either more or less efficient than single-stage contacting. However, two-stage contacting may have practical benefits in dealing with abrasive or flocculated dusts.

Some investigators have proposed, mostly on the basis of mathematical modeling, to optimize the design of scrubbers to obtain a given efficiency with a minimum power consumption (e.g., Goel and Hollands, op. cit.). In fact, no optimum in performance appears to exist; apart from some avoidable regions of unfavorable operation, increased contacting power yields increased efficiency.

Scrubber Performance Curves The scrubber performance curve, which shows the relationship of scrubber efficiency to the contacting power, has been found to take the form

$$N_t = \alpha P_T^{\gamma} \tag{17-8}$$

where α and γ are empirical constants that depend primarily on the aerosol (dust or mist) collected. In a log-log plot of N_t versus P_T, γ is the slope of the performance curve and α is the intercept at $P_T = 1$. Figure 17-46 shows such a performance curve for the collection of coal fly ash by a pilot-plant venturi scrubber (Raben "Use of Scrubbers for Control of Emissions from Power Boilers," United States–U.S.S.R. Symposium on Control of Fine-Particulate Emissions from Industrial Sources, San Francisco, 1974). The scatter in the data reflects not merely experimental errors but actual variations in the particle-size characteristics of the dust. Because the characteristics of an industrial dust vary with time, the scrubber performance curve necessarily must represent an average material, and the scatter in the data is frequently greater than is shown in Fig. 17-46. For best definition, the curve should cover as wide a range of contacting power as possible. Obtaining the data thus requires pilot-plant equipment with the flexibility to operate over a wide range of conditions. Because scrubber performance is not greatly affected by the size of the unit, it is feasible to conduct the tests with a unit handling no more than 170 m^3/h (100 ft^3/min) of gas.

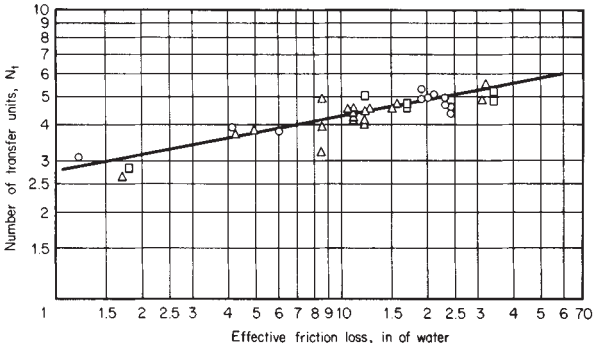


FIG. 17-46 Performance of pilot-plant venturi scrubber on fly ash. Liquid-to-gas ratio, gal/1000 ft^3: ○, 10; △, 15; □, 20. (*Raben, United States–U.S.S.R. Symposium on Fine-Particulate Emissions from Industrial Sources, San Francisco, 1974.*)

A clear interpretation of γ, the slope of the curve, is still lacking. Presumably, it should be related to the particle-size distribution of the dust. Because scrubbing preferentially removes the coarser particles, the fraction of the dust removed (or the increment of N_t) per unit of contacting power should decrease as the contacting power and efficiency increase, so that the value of γ should be less than unity. In fact, the value of γ has been less than unity for most dusts. Nevertheless, some data in the literature have displayed values of γ greater than unity when plotted on the transfer-unit basis, indicating that the residual fraction of dust became more readily collectible as contacting power and efficiency increased. More recent studies by Semrau et al. (EPA-650/2-74-108 and EPA-600/2-77-237) have revealed performance curves having two branches (typified by Fig. 17-47), the lower having a slope greater than unity and the upper a slope less than unity. This suggests that had the earlier tests been extended into higher contacting-power ranges, performance curves with flatter slopes might have appeared in those ranges.

Among the aerosols that gave performance curves with $\gamma > 1$, the only obvious common characteristic was that a large fraction of each was composed of submicrometer particles.

Cut-Power Correlation Another design method, also based on scrubber power consumption, is the cut-power method of Calvert [*J. Air Pollut. Control Assoc.*, **24,** 929 (1974); *Chem. Eng.*, **84**(18), 54 (1977)]. In this approach, the cut diameter (the particle diameter for which the collection efficiency is 50 percent) is given as a function of the gas pressure drop or of the power input per unit of volumetric gas flow rate. The functional relationship is presented as a log-log plot of the cut diameter versus the pressure drop (or power input). In principle, the function could be constructed by experimentally determining scrubber performance curves for discrete particle sizes and then plotting the particle sizes against the corresponding pressure drops necessary to give efficiencies of 50 percent. In practice, Calvert and coworkers evidently have in most cases constructed the cut-power functions for various scrubbers by modeling (Yung and Calvert, U.S. EPA-600/8-78-005b, 1978). They show a variety of curves, whereas empirical studies have indicated that different types of scrubbers generally have about the same performance at a given level of power consumption.

Condensation Scrubbing The collection efficiency of scrubbing can be increased by the simultaneous condensation of water vapor from the gas stream. Water-vapor condensation assists in particle removal by two entirely different mechanisms. One is the deposition of particles on cold-water droplets or other surfaces as the result of Stefan flow. The other is the condensation of water vapor on particles as nuclei, which enlarges the particles and makes them more readily collected by inertial deposition on droplets. Both mechanisms can operate simultaneously. However, for the buildup of particles by condensation to be effective, there must be adequate time for the particles to grow substantially before the principal gas-liquid-contacting operation takes place. Hence, if particle buildup is to be sought, the scrubber should be preceded by an appropriate gas-conditioning section. On the other hand, particle collection by Stefan flow can be induced simply by scrubbing the hot, humid gas with sufficient cold water to bring the gas below its initial dew point. Any practical method of inducing condensation on the dust particles will incidentally afford opportunities for the operation of the Stefan-flow mechanism. The hot gas stream must, of course, have a high initial moisture content, since the magnitude of the effects obtained is related to the quantity of water vapor condensed.

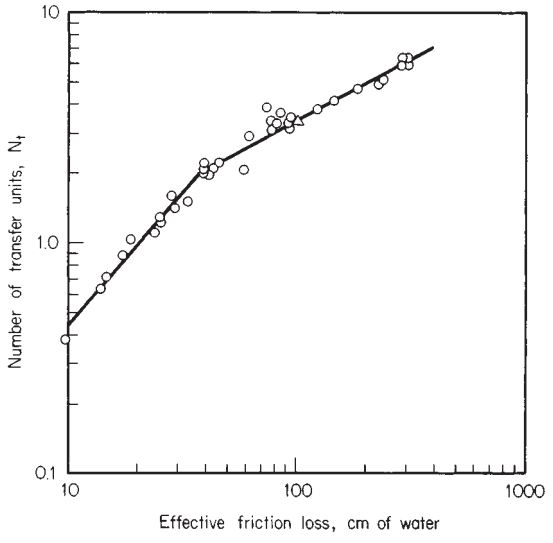


FIG. 17-47 Performance curve for orifice scrubber collecting ammonium fluorescin aerosol. (*Semrau et al., EPA 600/2-77-237, 1977.*)

Although there is a considerable body of literature on particle collection by condensation mechanisms, most of it is either theoretical or, if experimental, treats basic phenomena in simplified cases. Few studies have been made to determine what performance may be expected from condensation scrubbing under practical conditions in industrial applications. In a series of studies, Calvert and coworkers investigated several types of equipment for condensation scrubbing, generally emphasizing the use of the condensation center effect to build up the particles for collection by inertial deposition (Calvert and Parker, EPA-600/8-78-005c, 1978). From early estimates, they predicted that a condensation scrubber would require only about one-third or less of the power required by a conventional high-energy scrubber. A subsequent demonstration-plant scrubber system consisted of a direct-contact condensing tower fed with cold water followed by a venturi scrubber fed with recirculated water (Chmielewski and Calvert, EPA-600/7-81-148, 1981). The condensation and particle buildup took place in the cooling tower. In operation on humidified iron-foundry-cupola gas, this system still required about 65 percent as much power as for conventional high-energy scrubbing.

Semrau and coworkers [*Ind. Eng. Chem.*, **50,** 1615 (1958); *J. Air Pollut. Control Assoc.*, **13,** 587 (1963); EPA-650/2-74-108, 1974] investigated condensation scrubbing in pilot-plant studies in the field and, later, under laboratory conditions. Hot, humid gases were scrubbed directly with cold water under conditions that were favorable for the Stefan-flow mechanism but offered little or no opportunity for particle buildup. Some of the field studies indicated a contacting-power saving of as much as 50 percent for condensation scrubbing of Kraft-recovery-furnace fume. Laboratory tests on a predominantly submicrometer synthetic aerosol showed contacting-power savings of up to 40 percent with condensation scrubbing.

In the scrubbing of hot gases with high water content, condensation reduces contacting power and affords a direct power saving through the reduction of the gas volume by cooling and water-vapor condensation, but it incurs other costs for power and equipment for heat transfer and water cooling. However, condensation scrubbing may offer a net economic advantage if recovery of low-level heat is practical. It should also be advantageous when a hot gas must be not only cleaned but cooled and dehumidified as well; examples are the cleaning of blast-furnace gas for use as fuel and of SO_2-bearing waste gases for feed to a sulfuric acid plant.

Entrainment Separation The entrainment separator is a critical element of a scrubber, since the collection efficiency of the scrubber depends on essentially total removal of the spray from the gas stream. The sprays generated in scrubbers are generally large enough in droplet size that they can be readily removed by properly designed inertial separators. Primary collection of the spray is seldom the critical limitation on separator performance, but reentrainment is a common problem. In dust scrubbers it is essential that the entrainment separator not be of a form readily subject to blockage by solids deposits and that it be readily cleared of deposits if they should occur. Cyclone separators are advantageous in this respect and are widely used with venturi contactors. However, they cannot readily be made integral with scrubbers of some other configurations, which can be more conveniently fitted with various forms of impingement separators. Although separator design can be important, the most common

cause of reentrainment is simply the use of excessive gas velocities, and few data are available on the gas-handling capacities of separators. In the absence of good data, there is a frequent tendency to underdesign separators in an effort to reduce costs.

Venturi Scrubbers The venturi scrubber is one of the most widely used types of particulate scrubbers. The designs have become generally standardized, and units are manufactured by a large number of companies. Venturi scrubbers may be used as either high- or low-energy devices but are most commonly employed as high-energy units. The units originally studied and used were designed to the proportions of the classical venturis used for metering, but since it was discovered that these proportions have no special merits, simpler and more practical designs have been adopted. Most "venturi" contactors in current use are in fact not venturis but variable orifices of one form or another. Any of a wide range of devices can be used, including a simple pipe-line contactor. Although the venturi scrubber is not inherently more efficient at a given contacting power than other types of devices, its simplicity and flexibility favor its use. It is also useful as a gas absorber for relatively soluble gases, but because it is a cocurrent contactor, it is not well suited to absorption of gases having low solubilities.

Current designs for venturi scrubbers generally use the vertical downflow of gas through the venturi contactor and incorporate three features: (1) a "wet-approach" or "flooded-wall" entry section, to avoid dust buildup at a wet-dry junction; (2) an adjustable throat for the venturi (or orifice), to provide for adjustment of the pressure drop; and (3) a "flooded elbow" located below the venturi and ahead of the entrainment separator, to reduce wear by abrasive particles. The venturi throat is sometimes fitted with a refractory lining to resist abrasion by dust particles. The entrainment separator is commonly, but not invariably, of the cyclone type. An example of the "standard form" of venturi scrubber is shown in Fig. 17-48. The wet-approach entry section has made practical the recirculation of slurries. Various forms of adjustable throats, which may be under manual or automatic control,

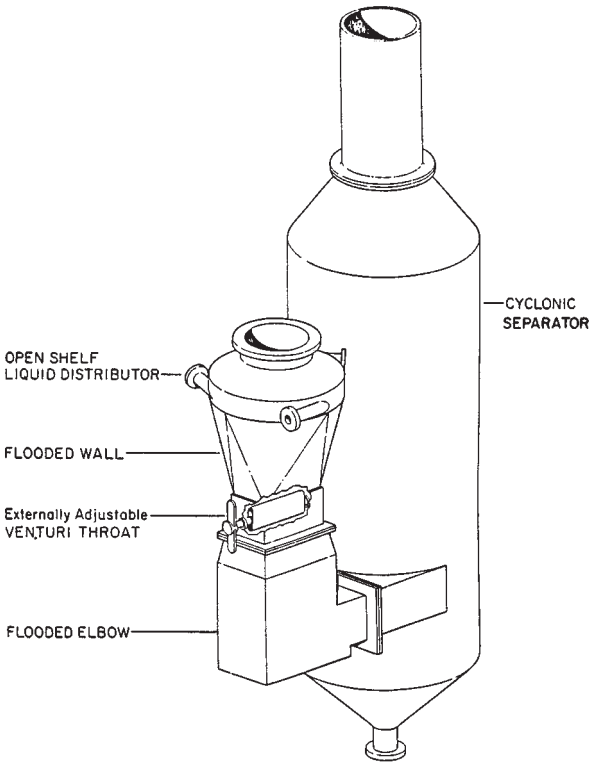


FIG. 17-48 Venturi scrubber. (*Neptune AirPol.*)

permit maintaining a constant pressure drop and constant efficiency under conditions of varying gas flow.

Self-Induced Spray Scrubbers Self-induced spray scrubbers form a category of gas-atomized spray scrubbers in which a tube or a duct of some other shape forms the gas-liquid-contacting zone. The gas stream flowing at high velocity through the contactor atomizes the liquid in essentially the same manner as in a venturi scrubber. However, the liquid is fed into the contactor and later recirculated from the entrainment separator section by gravity instead of being circulated by a pump as in venturi scrubbers. The scheme is well illustrated in Fig. 17-49*a*. A great many such devices using contactor ducts of various shapes, as in Fig. 17-49*b* are offered commercially. Although self-induced spray scrubbers can be built as high-energy units and sometimes are, most such devices are designed for only low-energy service.

The principal advantage of self-induced spray scrubbers is the elimination of a pump for recirculation of the scrubbing liquid. However, the designs for high-energy service are somewhat more complex and less flexible than those for venturi scrubbers.

Plate Towers Plate (tray) towers are countercurrent gas-atomized spray scrubbers using one or more plates for gas-liquid contacting. They are essentially the same as, if not identical to, the devices used for gas absorption and are frequently employed in applications in which gases are to be absorbed simultaneously with the removal of dust. Except possibly in cases in which condensation effects are involved, countercurrent operation is not significantly beneficial in dust collection.

The plates may be any of several types, including sieve, bubble-cap, and valve trays. The impingement baffle plate (Fig. 17-50) is commonly used for dust collection applications. Impingement on the baffles is not the controlling mechanism of particle collection; the principal collecting bodies are the droplets produced from the liquid by the gas as it flows through the perforations and around the baffles. The slot stage (Fig. 17-50) is in effect a miniature venturi contactor. Valve trays constitute multiple self-adjusting orifices that provide nearly constant gas pressure drop over considerable ranges of variation in gas flow. The gas pressure drop that can be taken across a single plate is necessarily limited, so that units designed for high contacting power must use multiple plates.

Plate towers are more subject to plugging and fouling than venturi-type scrubbers that have large passages for gas and liquid.

Packed-Bed Scrubbers Packed-bed scrubbers of the types used for gas absorption may also be used for dust collection but are subject to plugging by deposits of insoluble solids. Random packings, such as dumped Raschig rings and Berl saddles, are most seriously affected by plugging. Regular packings, such as stacked grids, are better in dust-collection service. When both a gas and particulate matter are to be collected, it is advisable to use a primary-stage scrubber of the venturi or similar type to collect the particulate matter ahead of a packed gas absorber.

Packed-bed scrubbers may be constructed for either vertical or horizontal gas flow. Vertical-flow units (packed towers) commonly use countercurrent flow of gas and liquid, although cocurrent flow is sometimes used. Packed scrubbers using horizontal gas flow usually employ cross-flow of liquid.

Scrubber packings are too large to serve as collecting bodies for any except very large dust particles. In the collection of fine particles, the packings serve primarily to promote fluid turbulence that aids the deposition of the dust particles on droplets. In a packed tower operating below the flooding point, with most of the liquid flowing in films and little spray formation, the relative efficiency in collection of particles may possibly be lower than that of a venturi-type scrubber operating at the same contacting power. However, no data are available to resolve the question.

Mobile-Bed Scrubbers Mobile-bed scrubbers (Fig. 17-51) are constructed with one or more beds of low-density spheres that are free to move between upper and lower retaining grids. The spheres are commonly 1.0 in (2.5 cm) or more in diameter and made from rubber or a plastic such as polypropylene. The plastic spheres may be solid or hollow. Gas and liquid flows are countercurrent, and the spherical packings are fluidized by the upward-flowing gas. The movement of

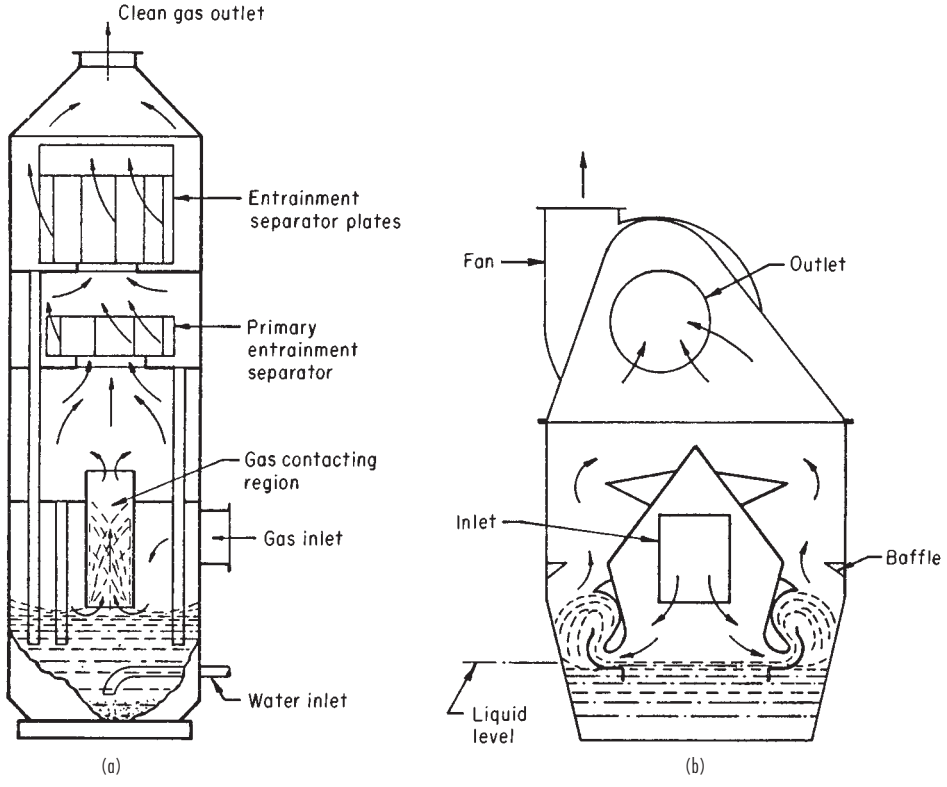


FIG. 17-49 Self-induced spray scrubbers. (*a*) Blaw-Knox Food & Chemical Equipment, Inc. (*b*) American Air Filter Co., Inc.

the packings is intended to minimize fouling and plugging of the bed. Mobile-bed scrubbers were first developed for absorbing gases from gas streams that also carry solid or semisolid particles.

The spherical packings are too large to serve as effective targets for the deposition of fine dust particles. In dust-collection service, the packings actually serve as turbulence promoters, while the dust particles are collected primarily by the liquid droplets.

The gas pressure drop through the scrubber may be increased by increasing the gas velocity, the liquid-to-gas ratio, the depth of the bed, the density of the packings, and the number of beds in series. In an experimental study, Yung et al. (EPA-600/7-79-071, 1979) determined that the collection efficiency of a mobile-bed scrubber was dependent only on the gas pressure drop and was not influenced independently by the gas velocity, the liquid-to-gas ratio, or the number of beds except as these factors affected the pressure drop. Yung et al. also reported that the mobile-bed scrubber was less efficient at a given pressure drop than scrubbers of the venturi type, but without offering comparable experimental supporting evidence.

Spray Scrubbers Spray scrubbers consist of empty chambers of some simple form in which the gas stream is contacted with liquid droplets generated by spray nozzles. A common form is a spray tower, in which the gas flows upward through a bank or successive banks of spray nozzles. Similar arrangements are sometimes used in spray chambers with horizontal gas flow. Such devices have very low gas pressure drops, and all but a small part of the contacting power is derived from the liquid stream. The required contacting power is obtained from an appropriate combination of liquid pressure and flow rate. Most spray scrubber are low-energy units. Collection of fine particles is possible but may require very high liquid-to-gas ratios, liquid feed pressures, or both. Plugging of the nozzles can be a persistent maintenance problem. Entrainment separators are necessary to prevent carry-over of spray into the exit gas.

Cyclone Scrubbers The vessels of cyclone scrubbers are all in the form of cyclones, which provide for entrainment separation. However, the gas-liquid-contacting devices may be of either the gas-atomized-spray or the preformed-spray type. The cyclone-spray scrubber shown in Fig. 17-52*a* has an axial spray tree, or manifold, equipped with hydraulic spray nozzles. Similar units are available with the spray nozzles mounted in the wall of the cyclone, discharging inward. This latter arrangement makes the nozzles more accessible for maintenance. In the cyclone scrubber shown in Fig. 17-52*b*, most of the gas-liquid contacting is accomplished in the swirl vanes, with the energy being supplied from the gas stream in the form of pressure drop. The swirl vanes serve the same function as do the trays in a tray tower. Higher contacting power can be provided by using additional sets of swirl vanes in series.

Ejector-Venturi Scrubbers In the ejector-venturi scrubber (Fig. 17-53) the cocurrent water jet from a spray nozzle serves both to scrub the gas and to provide the draft for moving the gas. No fan is required, but the equivalent power must be supplied to the pump that delivers water to the ejector nozzle. The water must be supplied in sufficient volume and at high enough pressure to provide both adequate draft and enough contacting power for the required scrubbing operation. Considered as a gas pump, the ejector is not a very efficient device, but the dissipated energy that is not effective in pumping does serve in gas-liquid contacting. The energy equivalent to any gas pressure rise across the scrubber is not part of the contacting power (Semrau et al., EPA-600/2-77-234, 1974).

The ejector-venturi scrubber is widely used as a gas absorber, but the combinations of water pressure and flow rate that are sufficient to provide the required draft usually do not also yield enough contacting power to give high collection efficiency on submicrometer particles. Other types of ejectors have been employed to provide higher contacting-power levels. In one, superheated water is discharged through

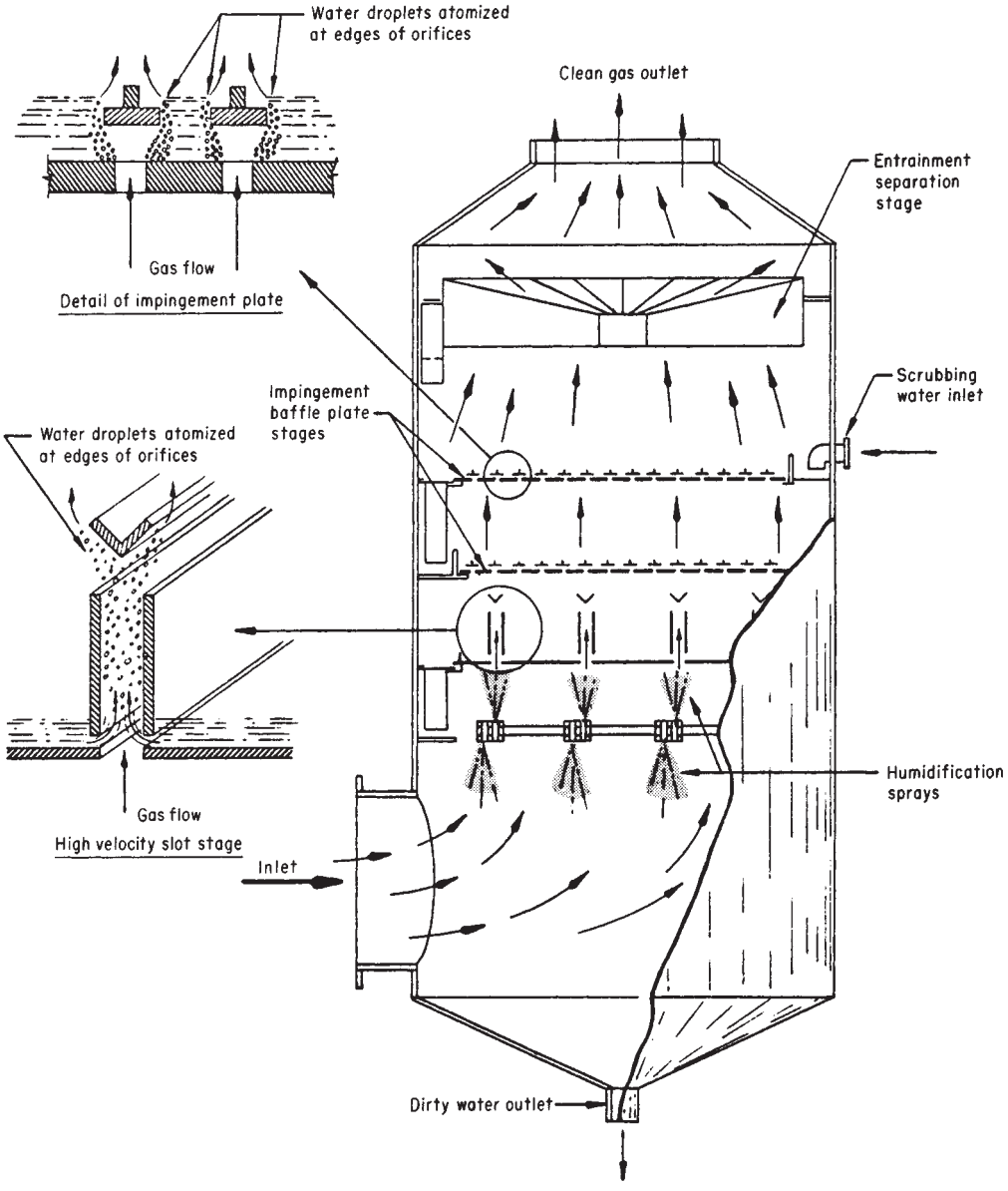


FIG. 17-50 Impingement-plate scrubber. (*Peabody Engineering Corp.*)

the nozzle, and part flashes to steam, increasing the mechanical energy available for scrubbing [Gardenier, *J. Air Pollut. Control Assoc.*, **24,** 954 (1974)]. Some units use two-fluid nozzles, with either compressed air or steam as the compressible fluid [Sparks, *J. Air Pollut. Control Assoc.*, **24,** 958 (1974)]. Most of the energy for gas movement and for atomizing the liquid and scrubbing the gas is derived from the compressed air or steam. In some ejector-venturi-scrubbers installations, part of the draft is supplied by a fan [Williams and Fuller, TAPPI, **60**(1), 108 (1977)].

Mechanical Scrubbers Mechanical scrubbers comprise those devices in which a power-driven rotor produces the fine spray and the contacting of gas and liquid. As in other types of scrubbers, it is the droplets that are the principal collecting bodies for the dust particles. The rotor acts as a turbulence producer. An entrainment separator must be used to prevent carry-over of spray. Among potential maintenance problems are unbalancing of the rotor by buildup of dust deposits and abrasion by coarse particles.

The simplest commercial devices of this type are essentially fans upon which water is sprayed. The unit shown in Fig. 17-54 is adapted to light duty, and heavy dust loads are avoided to minimize buildup on the rotor.

Fiber-Bed Scrubbers Fibrous-bed structures are sometimes used as gas-liquid contactors, with cocurrent flow of the gas and liquid streams. In such contactors, both scrubbing (particle deposition on droplets) and filtration (particle deposition on fibers) may take place. If only mists are to be collected, small fibers may be used, but if solid particles are present, the use of fiber beds is limited by the tendency of the beds to plug. For dust-collection service, the fiber bed must be composed of coarse fibers and have a high void fraction, so as to minimize the tendency to plug. The fiber bed may be made from metal or

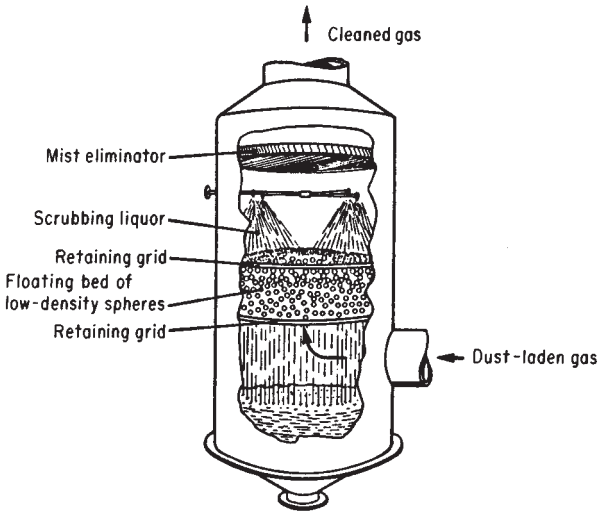


FIG. 17-51 Mobile-bed scrubber. (*Air Correction Division, UOP.*)

plastic fibers in the form of knitted structures, multiple layers of screens, or random-packed fibers. However, the bed must have sufficient dimensional stability so that it will not be compacted during operation.

Lucas and Porter (U.S. Patent 3,370,401, 1967) developed a fiber-bed scrubber in which the gas and scrubbing liquid flow vertically upward through a fiber bed (Fig. 17-55). The beds tested were composed of knitted structures made from fibers with diameters ranging from 89 to 406 μm. Lucas and Porter reported that the fiber-bed scrubber gave substantially higher efficiencies than did venturi-type scrubbers tested with the same dust at the same gas pressure drop. In similar experiments, Semrau (Semrau and Lunn, op. cit.) also found that a fiber-bed contactor made with random-packed steel-wool fibers gave higher efficiencies than an orifice contactor. However, there were indications that the fiber bed would have little advantage in the collection of submicrometer particles, presumably because of the large fiber size feasible for dust-collection service.

Despite their potential for increased collection efficiency, fiber-bed scrubbers have had only limited commercial acceptance for dust collection because of their tendency to become plugged. Their principal use has been in small units such as engine-intake-air cleaners, for which it is feasible to remove the fiber bed for cleaning at frequent intervals.

Electrically Augmented Scrubbers In some types of wet collectors, attempts are made to apply the electrostatic-deposition mechanism by charging the dust particles, the water droplets, or both. The objective is to combine in a scrubber high efficiency in collecting fine particles and the moderate power consumption characteristic of an electrical precipitator. Successful devices of this type have been essentially wet electrical precipitators and should properly be discussed in that category (see "Electrical Precipitators"). So far, there has been no clear demonstration of a device that combines the small size, compactness, and high efficiency of a high-energy scrubber with the relatively low power consumption of an electrical precipitator.

Dry Scrubbing *Dry scrubbing* is an umbrella term used to associate several different unit operations and types of hardware that can be used in combinations to accomplish the unit process of dry scrubbing. They all utilize scrubbing, in which mass transfer takes place between the gas phase and an active liquidlike surface, and they all discharge the resulting products separately as a gas and a solidlike "dry" product for reuse or disposal.

It is helpful to recognize three phases in the development of systems using dry scrubbing. The first phase used mainly good contactors and relatively expensive sorbents, which were tailored to catch targeted compounds with high efficiency (>99 percent). The second phase used mainly minimal contactors and cheap sorbents in order to get enough sulfur dioxide capture (>60 percent) to justify using cheaper higher sulfur coal. The third phase is ongoing; it uses mainly better contactors, sorbents, and fabric filters in order to get not only high SO_2 capture (>90 percent), but also substantial capture of other regulated emissions such as metals and dioxins.

The principle of dry scrubbing was first recognized by Lamb and Wilson [*I&EC*, **11**(5), 420 (1919)] and Wilson [*I&EC*, **12**(10), 1000 (1920)] at MIT during their World War I program to develop better

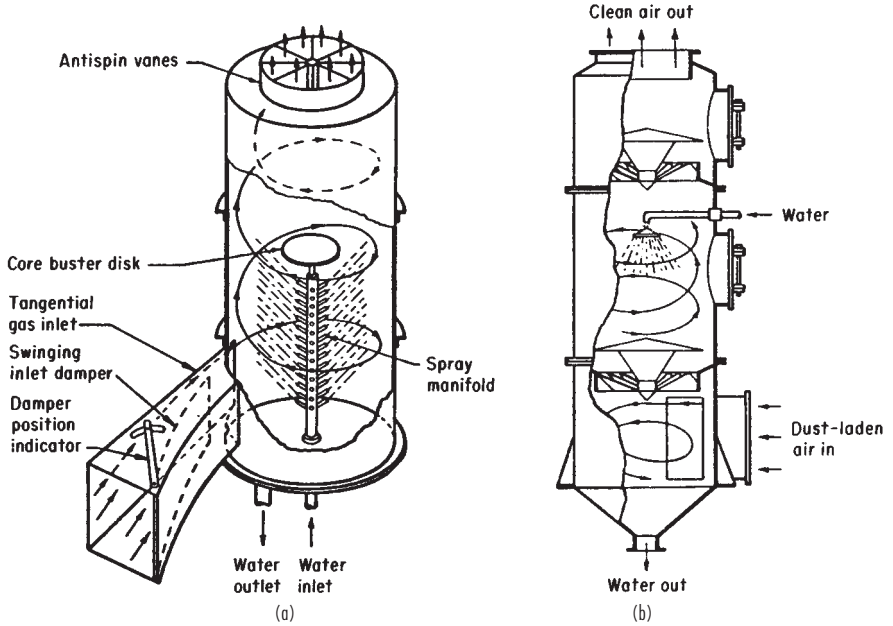


FIG. 17-52 Cyclone scrubbers. (*a*) Chemico Air Pollution Control Corp. (*b*) Ducon Co., Inc.

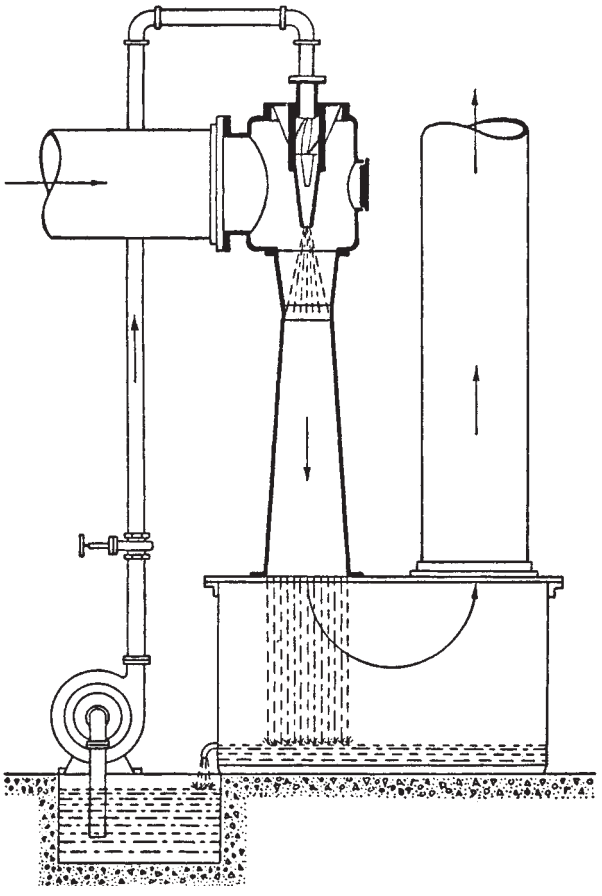


FIG. 17-53 Ejector-venturi scrubber. (*Schutte & Koerting Division, Amtek, Inc.*)

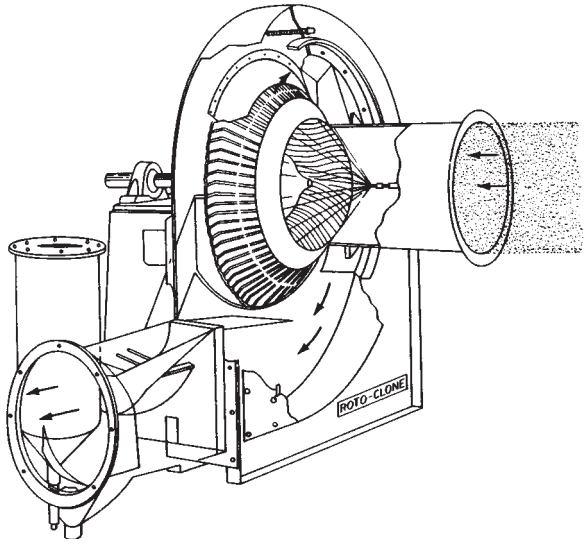


FIG. 17-54 Mechanical scrubber. (*American Air Filter Co., Inc.*)

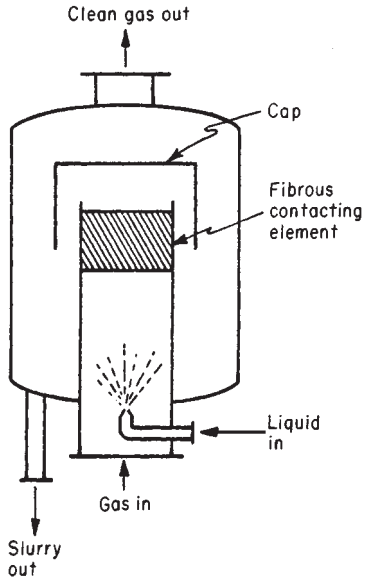


FIG. 17-55 Fibrous-bed scrubber. (*Lucas and Porter, U.S. Patent 3,370,401, 1967.*)

media for military gas masks. The preferred medium turned out to be a mixture of granular activated carbon with a new kind of porous granular hydrated lime, which they dubbed *activated soda-lime.* What activated it was a small but critical amount of sodium hydroxide, which was enough to maintain in use on French battlefields an equilibrium moisture film a few molecules thick on the surface of pores within lime particles. That film enhanced surface hydrolysis, diffusion, and neutralization of acid gases such as Cl_2 and SO_2, to the point that their removal became controlled by fast external gas-film diffusion, up to substantial utilization of the potential stoichiometric capacity. The better varieties of army activated soda-lime used in gas masks captured more than 99 percent of Cl_2 or SO_2 even after using up more than 10 percent of alkalinity. Gas-mask-canister sorbent beds typically used 8×14 mesh granules 10 cm deep, and tests were run with 1 percent acid gas at space velocities of 3000 to 7400 l/hr. Carbon dioxide was tested to higher penetrations; its capture was more than 50 percent even after using up more than 50 percent of available alkalinity.

With good dry scrubbing sorbents, the controlling resistance for gas cleaning is external turbulent diffusion, which also depends on energy dissipated by viscous and by inertial mechanisms. It turns out to be possible to correlate mass-transfer rate as a function of the friction factor.

It turns out that packed beds much less than a hundred particles thick behave as if they were well-stirred due to the entrance effect. Although it may seem odd that a packed bed can behave as if well-stirred, it typically takes at least a 100-particle bed depth in order for a plug-flow concentration wave to develop.

Integration of the Ergun equation for well stirred flow gives

$$\frac{C_2 - C_1}{C^\circ - C_2} = F_k \frac{\rho D_v (1 - \varepsilon_v) L}{\mu \varepsilon_v D_p} \tag{17-9}$$

Recognition of dry scrubbing as a mechanism useful in treating large gas flows first came in the 1960s as regulations were tightening on fly ash emissions from utility boilers. Dry scrubbing turns out to be the appropriate way to describe the interactions of sulfuric acid vapor with fly ash from pulverized coal combustion. On one hand, powdered sodium bicabonate was added to some flue gases in order to protect fabric filter bags from attack by sulfuric acid films on ash from high sulfur coal combustion. On the other hand, sulfur trioxide was added to other flue gases in order to generate sulfuric acid films that would improve the performance of electrostatic precipitators collecting inherently high resistivity ash from low sulfur coal. From Eq. (17-9),

it is readily apparent that the way to get more gas cleaning per unit pressure drop is to optimize the particle size and void fraction, and use relatively fewer particles operating at higher velocity. Such an arrangement runs out of stoichiometric capacity quickly, which leads naturally to transported bed contactors fed with fresh sorbent.

The actual name "dry scrubbing" was first publicized by Teller [U.S. Patent no. 3,721,066 (1973)]. He worked both with classical Army-type soda-lime and with his patented water-activated form of the alkaline feldspar nepheline syenite as a flow agent and feedstock sorbent for HF and SO_2 in hot, sticky fumes from glass melting furnaces. He claimed capture of more than 99 percent of 180 ppm HF and SO_2 for more than 20 hours in a packed bed of 200 × 325 mesh hydrated nepheline syenite at 42,000/hr.

Teller [U.S. Patent no. 3,997,652 (1976)] also patented a number of "chromatographic sorbents" using semivolatile liquid coatings similar to mobile phases used in capillary columns for gas chromatographs. For simple acid gases, Teller generally used a flash-drying-type venturi injector and pneumatic transport system to disperse fresh sorbent into hot gas to be treated and to provide time for turbulent mixing. He then typically used a baghouse to collect the loaded sorbent for inclusion with other feeds into the glass melting system.

Aluminum producers were also early users of another type of dry scrubbing for the difficult cleaning problem of acid gases in hot, sticky fumes from aluminum reduction potlines. Bazhenov et al. [*Tsvetn. Met.—Russia,* (6) 44 (1975)] described the use of a fluidized bed of feedstock aluminum oxide to clean potline offgas in an arrangement where there was an integral freeboard baghouse. Loaded sorbent was purged from the bed for feed into the aluminum reduction system. In that anhydrous system there was no water film as such inside the pores, but there was high specific surface, having liquidlike mobile active sites with a strong affinity for binding fluoride. The potential for achieving significant gas cleaning at very high space velocities led to dry scrubbing being applied both for incremental desulfurization of flue gases from coal-fired utility boilers and for removal of trace acid gases from solid waste incineration. A number of different hardware arrangements were tested all the way to full scale in order to determine accurately the various effects that must be optimized in order to achieve minimum net cost to be carried by the rate-paying public.

It was apparent from the very earliest tests that control of thin moisture films on the surface of reactive particles was the key to success. The main three competing arrangements, as compared by Statnick et al. [4th Annual Pitt. Coal Conf. (1987)] involved slurry spray dryers, where lime and water were injected together, versus systems where the gas was humidified by water injection before or after injection of limey dry powder reagents. It turns out that there are tradeoffs among the costs of hardware, reagent, and water dispersion and reagent purchase and disposal. Systems where water evaporates in the presence of active particles are usually less expensive overall.

The evaporation lifetimes of pure water droplets are described by Marshall and Seltzer [*CEP,* **46**(10), 501 and **46**(11), 575 (1950)] and by Duffie and Marshall [*CEP,* **49**(8), 417 (1953) and **49**(9), 480 (1953)]. Figure 17-56 is easy to use to estimate the necessary spray dispersion. For typical humidifier conditions of 300°F gas inlet temperature and a 20°F approach to adiabatic saturation at the outlet, a 60-micrometer droplet will require about 0.9 seconds to evaporate, while a 110-micrometer droplet will require about 3 seconds. If the time available for drying is no more than 3 seconds, it therefore follows that the largest droplets in a humidifier spray should be no larger than 100 micrometers. If the material being dried contains solids, droplet top size will need to be smaller due to slower evaporation rates. Droplets this small not only require considerable expensive power to generate, but since they have inherent penetration distances of less than a meter, they require expensive dispersion arrangements to get good mixing into large gas flows without allowing damp, sticky particles to reach walls.

The economics seem to be better for systems where dry powdered fresh lime plus ground recycled lime is injected along with a relatively coarse spray which impinges on and dries out from the reagent, as described by Stouffer et al. [*I&EC Res.,* **28**(1) 20 (1989)]. Withum et al. [9th Ann. Pitt. Coal Prep. Util. Env. Control Contractors Conf. (1993)] describes an advanced version of that system that has been further optimized to the point that it is competitive with wet limestone scrubbing for >90 percent flue gas desulfurization.

The most popular dry scrubbing systems for incinerators have involved the spray drying of lime slurries, followed by dry collection in electrostatic precipitators or fabric filters. Moller and Christiansen [Air Poll. Cont. Assoc. 84-9.5 (1984)] published data on early European technology. Moller et al. [U.S. Patent no. 4,889,698 (1989)] describe the newer extension of that technology to include both spray-dryer absorption and dry scrubbing with powdered, activated carbon injection. They claim greatly improved removal of mercury, dioxins, and NOx.

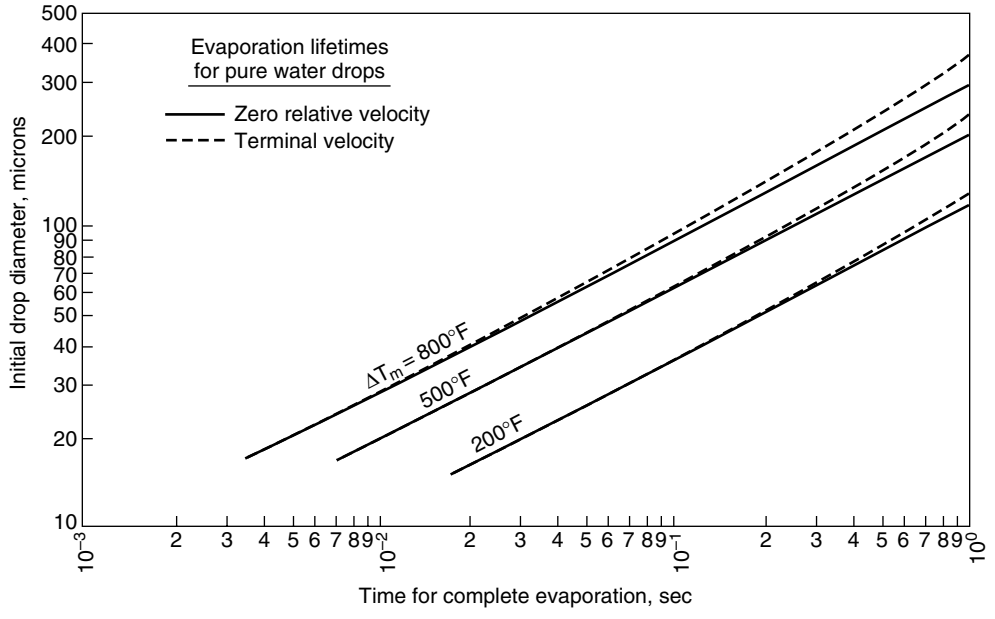


FIG. 17-56 Effect of drop diameter on time for complete evaporation of water drops.

Optimized modern dry scrubbing systems for incinerator gas cleaning are much more effective (and expensive) than their counterparts used so far for utility boiler flue gas cleaning. Brinckman and Maresca [ASME Med. Waste Symp. (1992)] describe the use of dry hydrated lime or sodium bicarbonate injection followed by membrane filtration as preferred treatment technology for control of acid gas and particulate matter emissions from modular medical waste incinerators, which have especially high dioxin emissions.

Kreindl and Brinckman [Air Waste Man. Assoc., paper 93-RP-154.04 (1993)] describe the three conventional flue-gas cleaning-process concepts (standard dry scrubbing, quasi-dry scrubbing, and wet scrubbing) as being inherently inadequate to meet the emerging European incinerator metal and organic emissions limits. Standard dry scrubbing can be upgraded by using powdered carbon along with lime, and switching to membrane filter media. Quasi-dry scrubbing can be upgraded by using powdered carbon along with lime spray drying [as also described by Moller (1989)], and switching to membrane filter media. Wet scrubbing can be upgraded by post-treatment following the wet scrubber with a circulating fluidized bed of granular activated carbon, again followed by a membrane filter.

Control of metal and organic emissions by dry scrubbing involves more than the simple acid gas neutralization discussed so far. Capture of metals other than mercury is mainly a matter of using a fabric filter having the capability of retaining unagglomerated submicron particles that are relatively enriched in toxic metals such as cadmium. Use of membrane-coated filter media is almost essential to do that well. Capture of mercury and dioxins is mainly achieved with activated carbon, which is more effective when used in combination with chlorine inhibitors. Karasek [U.S. Patent no. 4,793,270 (1988)] describes the inhibiting effects of sulfur compounds, which is why dioxins are rarely a problem in flue gases from coal-fired combustion. Naikwadi and Karasek [*Chemosphere,* **27**(1–3), 335 (1993)] describe the potent inhibiting effect of amines. That is presumably why German experience is finding that dioxins are rarely a problem in flue gases that have undergone some form of ammonia deNOx treatment, as described by Hahn [*Chemosphere,* **25**(1–2), 57 (1992)]. Hahn, like Kreindl and Brinckman, also argues that classical wet scrubbers will need to be upgraded with modern dry scrubbers and fabric filters.

Fabric Filters Fabric filters, commonly termed "bag filters" or "baghouses," are collectors in which dust is removed from the gas stream by passing the dust-laden gas through a fabric of some type (e.g., woven cloth, felt, or porous membrane). These devices are "surface" filters in that dust collects in a layer on the surface of the filter medium, and the dust layer itself becomes the effective filter medium. The pores in the medium (particularly in woven cloth) are usually many times the size of the dust particles, so that collection efficiency is low until sufficient particles have been collected to build up a "precoat" in the fabric pores (Billings and Wilder, *Handbook of Fabric Filter Technology,* vol. I, EPA No. APTD-0690, NTIS No. PB-200648, 1979). During this initial period, particle deposition takes place mainly by inertial and flow-line interception, diffusion, and gravity. Once the dust layer has been fully established, sieving is probably the dominant deposition mechanism, penetration is usually extremely low except during the fabric-cleaning cycle, and only limited additional means remain for influencing collection efficiency by filter design. Filter design is related mainly to choices of gas filtration velocities and pressure drops and of fabric-cleaning cycles.

Because of their inherently high efficiency on dusts in all particle-size ranges, fabric filters have been used for collection of fine dusts and fumes for over 100 years. The greatest limitation on filter application has been imposed by the temperature limits of available fabric materials. The upper limit for natural fibers is about 90°C (200°F). The major new developments in filter technology that have been made since 1945 have followed the development of fabrics made from glass and synthetic fibers, which has extended the temperature limits to about 230 to 260°C (450 to 500°F). The capabilities of available fibers to resist high temperatures are still among the most severe limitations on the possible applications of fabric filters.

Gas Pressure Drops The filtration, or superficial face, velocities used in fabric filters are generally in the range of 0.3 to 3 m/min (1 to 10 ft/min), depending on the types of fabric, fabric supports, and cleaning methods used. In this range, gas pressure drops conform to Darcy's law for streamline flow in porous media, in which the pressure drop is directly proportional to the flow rate. The pressure drop across the fabric and the collected dust layer may be expressed (Billings and Wilder, op. cit.) by

$$\Delta p = K_1 V_f + K_2 w V_f \tag{17-10}$$

where Δp = kPa, or in of water; V_f = superficial velocity through filter, m/min, or ft/min; w = dust loading on filter, g/m^2, or lbm/ft^2; and K_1 and K_2 are resistance coefficients for the "conditioned" fabric and the dust layer respectively. The conditioned fabric is that fabric in which a relatively consistent dust load remains deposited in depth following cycles of filtration and cleaning. K_1, expressed in units of kPa/(m/min) or in water/(ft/min), may be more than 10 times the value of the resistance coefficient for the original clean fabric. If the depth of the dust layer on the fabric is greater than about 0.2 cm (1/16 in), corresponding to a fabric dust loading on the order of 500 g/m^2 (0.1 lbm/ft^2), the pressure drop across the fabric (including the dust in the pores) is usually negligible relative to that across the dust layer.

The specific resistance coefficient for the dust layer K_2 was originally defined by Williams et al. [*Heat. Piping Air Cond.,* **12,** 259 (1940)], who proposed estimating values of the coefficient by use of the Kozeny-Carman equation [Carman, *Trans. Inst. Chem. Eng. (London),* **15,** 150 (1937)]. In practice, K_1 and K_2 are measured directly in filtration experiments. The K_1 and K_2 values can be corrected for temperature by multiplying by the ratio of the gas viscosity at the desired condition to the gas viscosity at the original experimental conditions. Values of K_2 determined for certain dusts by Williams et al. (op. cit.) are presented in Table 17-5.

Lapple (in Perry, *Chemical Engineers' Handbook,* 3d ed., McGraw-Hill, New York, 1950) presents an alternative form of Eq. (17-10) in which the gas-viscosity term is explicit instead of being incorporated into the resistance coefficients:

$$\Delta p_i = K_c \mu V_f + K_d \mu w V_f \tag{17-11}$$

where Δp_i = in water, μ = cP, V_f = ft/min, w = gr/ft^2, K_c = cloth resistance coefficient = (in water)/(cP)(ft/min), and K_d = dust-layer resistance coefficient = (in water)/(cP)(gr/ft^2)(ft/min). K_d may be expressed in the same units, using the Kozeny-Carman equation:

$$K_d = \frac{160.0(1-\varepsilon_v)}{\phi_s^2 D_p^2 \rho_s \varepsilon_v^3} \tag{17-12}$$

where D_p = μm and ρ_s = lbm/ft^3.

Data sufficient to permit reasonable predictions of K_d from Eq. (17-12) are seldom available. The range in the values of K_d that may be encountered in practice is illustrated in Fig. 17-57 in which avail-

TABLE 17-5 Specific Resistance Coefficients for Certain Dusts*

Dust	K_2† for particle size less than						
	20 mesh	140 mesh	375 mesh	90 μm	45 μm	20 μm	2 μm
Granite	1.58	2.20				19.8	
Foundry	0.62	1.58	3.78				
Gypsum			6.30			18.9	
Feldspar			6.30			27.3	
Stone	0.96			6.30			
Lampblack							47.2
Zinc oxide							15.7‡
Wood				6.30			
Resin (cold)		0.62				25.2	
Oats	1.58			9.60	11.0		
Corn	0.62		1.58	3.78	8.80		

*Data from Williams et al., *Heat. Piping Air Cond.,* **12,** 259–263 (1940).

†$K_2 = \dfrac{\Delta p_i}{V_f w}, \dfrac{\text{in water}}{(\text{ft/min})(\text{lbm/ft}^2)}$.

NOTE: These data were obtained when filtering air at ambient conditions. For gases other than atmospheric air, the Δp_i values predicted from Table 17-5 should be multiplied by the actual gas viscosity divided by the viscosity of atmospheric air.

‡Flocculated material not dispersed; size actually larger.

able experimental determinations of K_d reported in the literature for a variety of dusts are plotted against particle size. In most cases no accurate particle-size data were reported, and the curves represent the estimated range of particle size involved. The data of Williams et al. (op. cit.) are related to a wide variety of dusts, and only the approximate limits enclosing these data are shown. Also included are curves predicted from Eq. (17-12) for specific values of ϕ_s, ρ_s, and ε_v. It is apparent from these curves that smaller particles tend toward higher values of ε_v, which is consistent with the observation that fine dusts (particularly those smaller than 10 μm) have lower bulk densities than coarser fractions, apparently because of the effects of surface forces. For coarse dusts, K_d varies approximately inversely as the square of the particle diameter, which implies that the void fraction (or bulk density) does not change with particle size. However, for particles finer than 10 μm, the value of K_d appears to become constant, increased voids compensating for the reduction in size. In addition to the increased voidages encountered with small particles, slip flow also contributes to the relative constancy of the experimental values of K_d for particle sizes under 5 μm.

Because of the assumptions underlying its derivation, the Kozeny-Carman equation is not valid at void fractions greater than 0.7 to 0.8 (Billings and Wilder, op. cit.). In addition, in situ measurement of the void fraction of a dust layer on a filter fabric is extremely difficult and has seldom even been attempted. The structure of the layer is dependent on the character of the fabric surface as well as on the characteristics of the dust, whereas the application of Eq. (17-12) implicitly assumes that K_2 is dependent only on the properties of the dust. A smooth fabric surface permits the dust to become closely packed, leading to a relatively high value of K_2. If the surface is napped or has numerous extended fibrils, the dust cake formed will be more porous and have a lower value of K_2 [Billings and Wilder, op. cit.; Snyder and Pring, *Ind. Eng. Chem.*, **47,** 960 (1955); and K. T. Semrau, unpublished data, SRI International, Menlo Park, Calif., 1952–1953].

Equation (17-10) indicates that for filtration at a given velocity the pressure drop is a linear function of the fabric dust loading w. In some cases, particularly with smooth-surfaced fabrics, this is at least approximately the case, but in other instances the function displays an upward curvature with increases in w, indicating compression of the dust layer, the fabric, or both, and a consequent increase in K_2 (Snyder and Pring, op. cit.; Semrau, op. cit.). Several investigations have shown K_2 to be increased by increases in the filtration velocity [Billings and Wilder, op. cit.; Spaite and Walsh, *Am. Ind. Hyg. Assoc. J.*, **24,** 357 (1968)]. However, the various investigators do not agree on the magnitude of the velocity effects. Billings and Wilder suggest assuming as an approximation that K_2 is directly proportional to the filtration velocity, but the actual relationship is probably dependent on the nature of the fabric and fabric surface, the characteristics of the dust, the dust loading on the fabric, and the pressure drop.

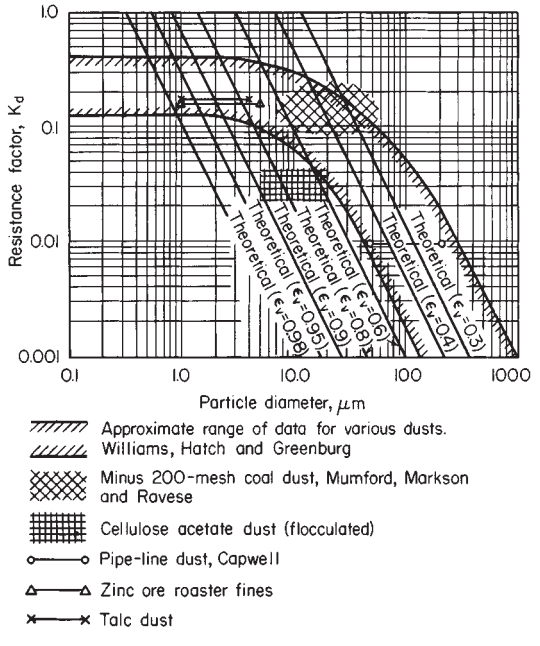


FIG. 17-57 Resistance factors for dust layers. Theoretical curves given are based on Eq. (20-78) for a shape factor of 0.5 and a true particle specific gravity of 2.0. [*Williams, Hatch, and Greenburg,* Heat. Piping Air. Cond., ***12,*** *259 (1940); Mumford, Markson, and Ravese,* Trans. Am. Soc. Mech. Eng., ***62,*** *271 (1940); Capwell, Gas,* ***15,*** *31 (August 1939)*].

Clearly, the factors determining K_2 are far more complex than is indicated by a simple application of the Kozeny-Carman equation, and when possible, filter design should be based on experimental determinations made under conditions approximating those expected in the planned installation.

Types of Filters Current fabric-filter designs fall into three types, depending on the method of cleaning used: (1) shaker-cleaned, (2) reverse-flow-cleaned, and (3) reverse-pulse-cleaned. The shaker-cleaned filter is the earliest form of bag filter (Fig. 17-58). The open lower ends of the bags are fastened over openings in the tube sheet that separates the lower dirty-gas inlet chamber from the upper clean-gas chamber. The bag supports from which the bags are suspended are connected to a shaking mechanism. The dirty gas flows upward into the filter bags, and the dust collects on the inside surfaces of the bags. When the gas pressure drop rises to a chosen upper limit as the result of dust accumulation, the gas flow is stopped and the shaker is operated, giving a whipping motion to the bags. The dislodged dust falls into the dust hopper located below the tube sheet. If the filter is to be operated continuously, it must be constructed with multiple compartments, so that the individual compartments can be sequentially taken off line for cleaning while the other compartments continue in operation (Fig. 17-59).

Shaker-cleaned filters are available as standard commercial units, although large baghouses for heavy-duty service are commonly custom-designed and -fabricated. The oval or round bags used in the standard units are usually 12 to 20 cm (5 to 8 in) in diameter and 2.5 to 5 m (8 to 17 ft) long. The large, heavy-duty baghouses may use bags up to 30 cm (12 in) in diameter and 9 m (30 ft) long. The bags must be made of woven fabrics to withstand the flexing and stretching involved in shaking. The fabrics may be made from natural fibers (cotton or wool) or synthetic fibers. Fabrics of glass or mineral fibers are generally too fragile to be cleaned by shaking and are usually used in reverse-flow-cleaned filters.

Large units (other than custom units) are usually built up of standardized rectangular sections in parallel. Each section contains on the order of 1000 to 2000 ft^2 of cloth, and the sections are assembled in the field to form a single filter housing. In this manner, the filter can be partitioned so that one or more sections at a time can be cut out of service for shaking or general maintenance.

Ordinary shaker-cleaned filters may be shaken every ¼ to 8 h, depending on the service. A manometer connected across the filter is useful in determining when the filter should be shaken. Fully automatic filters may be shaken as frequently as every 2 min, but bag maintenance will be greatly reduced if the time between shakings can be increased to 15 or 20 min without developing excessive pressure drop. Cleaning may be actuated automatically by a differential-pressure switch. It is essential that the gas flow through the filter be stopped when shaking in order to permit the dust to fall off. With very fine dust, it may even be necessary to equalize the pressure across the cloth [Mumford, Markson, and Ravese, *Trans. Am. Soc. Mech. Eng.*, **62,** 271 (1940)]. In practice this can be accomplished without interrupting the operation by cutting one section out of service at a time, as shown in Fig. 17-59. In automatic filters this operation involves closing the dampers, shaking the filter units either pneumatically or mechanically, sometimes with the addition of a reverse flow of cleaned gas through the filter, and lastly reopening the dampers. For compressed-air-operated automatic filters, this entire operation may take only 2 to 10 s. For ordinary mechanical filters equipped for automatic control, the operation may take as long as 3 min.

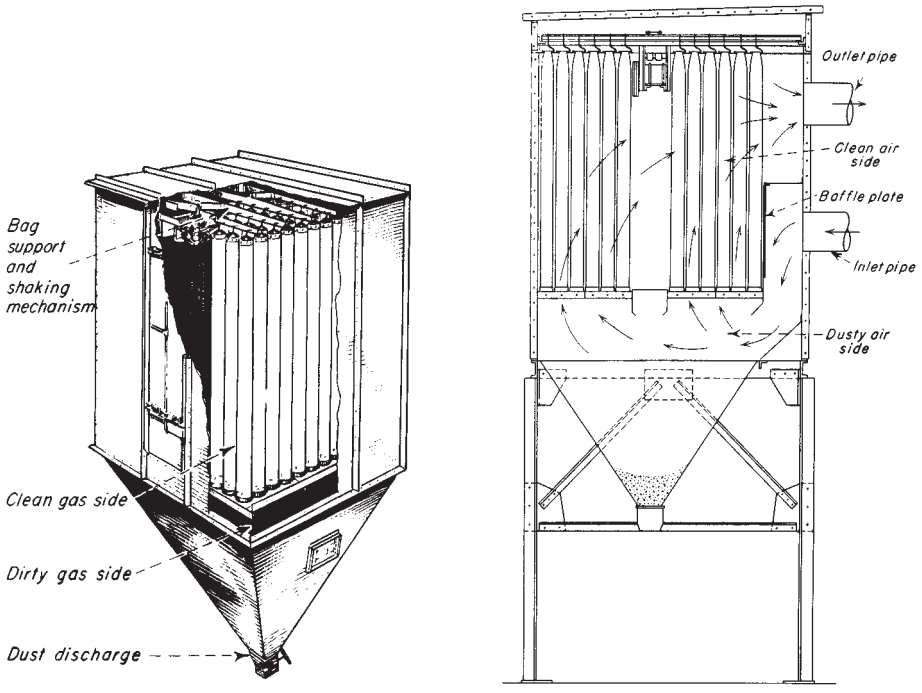


FIG. 17-58 Typical shaker-type fabric filters. (*a*) Buell Norblo (cutaway view). (*b*) Wheelabrator-Frye Inc. (sectional view).

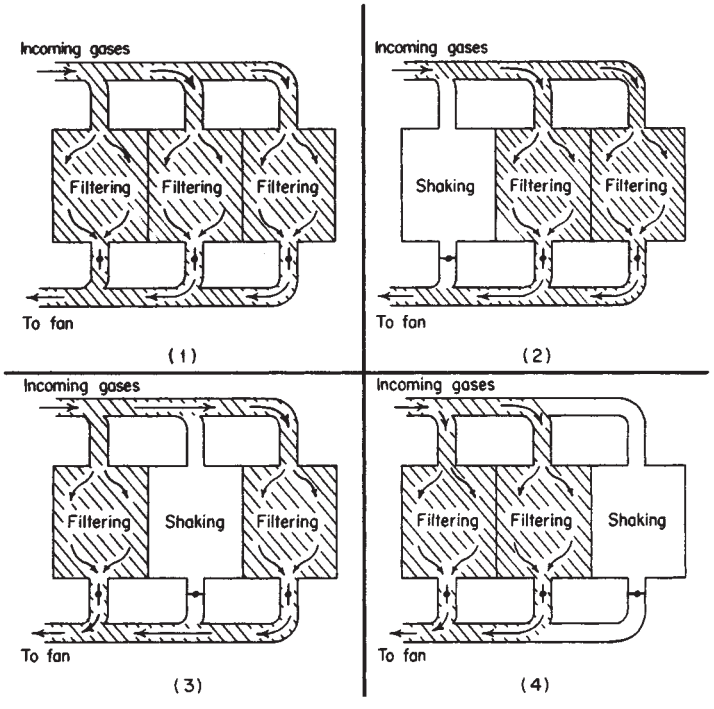


FIG. 17-59 Three-compartment bag filter at various stages in the cleaning cycle. (*Wheelabrator-Frye Inc.*)

Equation (17-11) may be rewritten as

$$\Delta p_i = K_d \mu c_d V_f^2 t_m \qquad (17\text{-}13)$$

where c_d = dust concentration in dirty gas, gr/ft^3; and t_m = filtration time, min. This shows that the pressure drop due to dust accumulation varies as the square of the gas velocity through the filter. (The actual effect of velocity on pressure drop may be even greater in some instances.) Greater cloth area and reduced filtration velocity therefore afford substantial reductions in shaking frequency and in bag wear. Consequently, it is generally economical to be conservative in specifying cloth area. Shaker-cleaned filters are generally operated at filtration velocities of 0.3 to 2.5 m/min (1 to 8 ft/min) and at pressure drops of 0.5 to 1.5 kPa (2 to 6 in water). For very fine dusts or high dust concentrations, filtration velocities should not exceed 1 m/min (3 ft/min). For fine fumes and dusts in heavy-duty installations, filtration velocities of 0.3 to 0.6 m/min (1 to 2 ft/min) have long been accepted on the basis of operating experience.

Cyclone precleaners are sometimes used to reduce the dust load on the filter or to remove large hot cinders or other materials that might damage the bags. However, reducing the dust load on the filter by this means may not reduce the pressure drop, since the increase in K_2 produced by the reduction in average particle size may compensate for the decrease in the fabric dust loading.

In filter operation, it is essential that the gas be kept above its dew point to avoid water-vapor condensation on the bags and resulting plugging of the bag pores. However, fabric filters have been used successfully in steam atmospheres, such as those encountered in vacuum dryers. In such cases, the housing is generally steam-traced.

Reverse-flow-cleaned filters are generally similar to the shaker-cleaned filters except for the elimination of the shaker. After the flow of dirty gas has stopped, a fan is used to force clean gas through the bags from the clean-gas side. This flow of gas partly collapses the bags and dislodges the collected dust, which falls to the dust hopper. Rings are usually sewn into the bags at intervals along the length to prevent complete collapse, which would obstruct the fall of the dislodged dust. The principal applications of reverse-flow cleaning are in units using fiberglass fabric bags for dust collection at temperatures above 150°C (300°F). Collapsing and reinflation of the bags can be made sufficiently gentle to avoid putting excessive stresses on the fiberglass fabrics [Perkins and Imbalzano, "Factors Affecting the Bag Life Performance in Coal-Fired Boilers," 3d APCA Specialty Conference on the User and Fabric Filtration Equipment, Niagara Falls, N.Y., 1978; and Miller, *Power,* **125**(8), 78 (1981)]. As with shaker-cleaned filters, compartments of the baghouse are taken off line sequentially for bag cleaning. The gas for reverse-flow cleaning is commonly supplied in an amount necessary to give a superficial velocity through the bags of 0.5 to 0.6 m/min (1.5 to 2.0 ft/min), which is the same range as the filtration velocities frequently used.

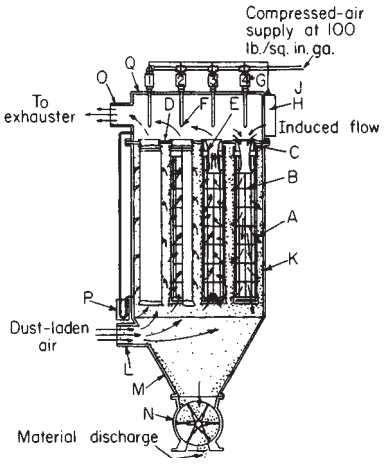


FIG. 17-60 Reverse-pulse fabric filter: (*a*) filter cylinders; (*b*) wire retainers; (*c*) collars; (*d*) tube sheet; (*e*) venturi nozzle; (*f*) nozzle or orifice; (*g*) solenoid valve; (*h*) timer; (*j*) air manifold; (*k*) collector housing; (*l*) inlet; (*m*) hopper; (*n*) air lock; (*o*) upper plenum. (*Mikropul Division, U.S. Filter Corp.*)

In the reverse-pulse filter (frequently termed a reverse-jet filter), the filter bag forms a sleeve that is drawn over a wire cage, which is usually cylindrical (Fig. 17-60). The cage supports the fabric on the clean-gas side, and the dust is collected on the outside of the bag. A venturi nozzle is located in the clean-gas outlet from the bag. For cleaning, a jet of high-velocity air is directed through the venturi nozzle and into the bag, inducing a flow of cleaned gas to enter the bag and flow through the fabric to the dirty-gas side. The high-velocity jet is released in a sudden, short pulse (typical duration 100 ms or less) from a compressed-air line by a solenoid valve. The pulse of air and clean gas expands the bag and dislodges the collected dust. Rows of bags are cleaned in a timed sequence by programmed operation of the solenoid valves. The pressure of the pulse is sufficient to dislodge the dust without cessation of the gas flow through the filter unit.

It has been a common practice to clean the bags on line (i.e., without stopping the flow of dirty gas into the filter), and reverse-pulse bag filters have been built without division into multiple compartments. However, investigations [Leith et al., *J. Air Pollut. Control Assoc.,* **27,** 636 (1977)] and experience have shown that, with online cleaning of reverse-pulse filters, a large fraction of the dust dislodged from the bag being cleaned may redeposit on neighboring bags rather than fall to the dust hopper. As a result, there is a growing trend to off-line cleaning of reverse-pulse filters. The baghouse is sectionalized so that the outlet-gas plenum serving the bags in a section can be closed off from the clean-gas exhaust, thereby stopping the flow of inlet gas through the bags. On the dirty-gas side of the tube sheet, the bags of the section are separated by partitions from the neighboring sections, where filtration is continuing. Sections of the filter are cleaned in rotation, as in shaker and reverse-flow filters.

Some manufacturers are using relatively low-pressure air (100 kPa, or 15 lbf/in^2, instead of 690 kPa, or 100 lbf/in^2) and are eliminating the venturi tubes for clean-gas induction. Others have eliminated the separate jet nozzles located at the individual bags and use a single jet to inject a pulse into the outlet-gas plenum.

Reverse-pulse filters are typically operated at higher filtration velocities (air-to-cloth ratios) than shaker or reverse-flow filters designed for the same duty. Filtration velocities may range from 1 to 4.5 m/min (3 to 15 ft/min), depending on the dust being collected, but for most dusts the commonly used range is about 1.2 to 2.5 m/min (4 to 8 ft/min). The frequency of cleaning is also dependent on the nature and concentration of the dust, with the intervals between pulses varying from about 2 to 15 min.

The cleaning action of the pulse is so effective that the dust layer may be completely removed from the surface of the fabric. Consequently, the fabric itself must serve as the principal filter medium for at least a substantial part of the filtration cycle. Woven fabrics are unsuitable for such service, and felts of various types must be used. The bulk of the dust is still removed in a surface layer, but the felt ensures that an adequate collection efficiency is maintained until the dust layer has formed.

Filter Fabrics The cost of the filter bags represents a substantial part of the erected cost of a bag filter—typically 5 to 20 percent, depending on the bag material [Reigel and Bundy, *Power,* **121**(1), 68 (1977)]. The cost of bag repair and replacement is the largest component of the cost of bag-filter maintenance. Consequently, the proper choice of filter fabric is critical to both the technical performance and the economics of operating a filter. With the advent of synthetic fibers, it has become possible to produce fabrics having a wide range of properties. However, demonstrating the acceptability of a fabric still depends on experience with prolonged operation under the actual or simulated conditions of the proposed application. The choice of a fabric material for a given service is necessarily a compromise, since no single material possesses all the properties that may be desired. Following the choice of material, the type of fabric construction is critical.

Two principal types of fabric are adaptable to filter use: woven fabrics, which are used in shaker and reverse-flow filters; and felts, which are used in reverse-pulse filters. The felts made from synthetic fibers are needle felts (i.e., felted on a needle loom) and are normally rein-

forced with a woven insert. The physical properties and air permeabilities of some typical woven and felt filter fabrics are presented in Tables 17-6 and 17-7. The "air permeability" of a filter fabric is defined as the flow rate of air in cubic feet per minute (at 70°F, 1 atm) that will pass through 1 ft^2 of clean fabric under an applied differential pressure of ½ in water. The resistance coefficient K_F of the clean fabric is defined by the equation in Table 17-6, which may be used to calculate the value of K_F from the air permeability. If Δp_i is taken as 0.5 in water, μ as 0.0181 cP (the viscosity of air at 70°F and 1 atm), and V_f as the air permeability, then $K_F = 27.8$/air permeability.

Collection Efficiency The inherent collection efficiency of fabric filters is usually so high that, for practical purposes, the precise level has not commonly been the subject of much concern. Furthermore, for collection of a given dust, the efficiency is usually fixed by the choices of filter fabric, filtration velocity, method of cleaning, and cleaning cycle, leaving few if any controllable variables by which efficiency can be further influenced. Inefficiency usually results from bags that are poorly installed, torn, or stretched from excessive dust loading and pressure drop. Of course, certain types of fabrics may simply be unsuited for filtration of a particular dust, but usually this will soon become obvious.

Few basic studies of the efficiency of bag filters have been made. Increased dust penetration immediately following cleaning has been readily observed while the dust layer is being reestablished. However,

TABLE 17-6 Resistance Factors and Air Permeabilities for Typical Woven Fabrics

Cloth	Pore size,* in	Threads/in	Weight, oz/yd^2	Thread* diameter, in	K_F†	Air permeability, (ft^3/min)/ft^2 at Δp_i = ½ in H_2O
Osnaburg cotton	0.01	32 × 28		0.02	0.51	55
Osnaburg cotton (soiled)‡		32 × 28			4.80	5.8
Drill cotton	0.01	68 × 40	5.28	0.01	0.093	300
Cotton§		46 × 56			1.39	20
Cotton§		104 × 68			1.54	18
Cotton sateen (unnapped)	0.007	96 × 56	6.88	0.009	0.27	103
Cotton sateen (unnapped)	0.005	96 × 64	8.23	0.01	0.88	32
Cotton sateen (unnapped)		96 × 60		0.012	1.63	17
Cotton sateen (unnapped)	0.004	96 × 56	10.2	0.011	1.12	25
Wool					0.25	111
Wool		40 × 50	11.5	0.014	0.33	84
Wool, white§		36 × 32			0.15	185
Wool, black§		28 × 30			0.25	110
Wool§		30 × 26			0.51	55
Vinyon§		37 × 37			0.12	23
Nylon tackle twill		72 × 196		0.010	0.66	42
Nylon sailcloth		130 × 130		0.007	1.66	17
Nylon§		37 × 37			1.74	16
Nylon§					3.71	7.5
Asbeston§					0.56	50
Orlon§		72 × 72			0.66	42
Orlon§		74 × 38			0.75	37
Orlon§					1.16	24
Orlon§					1.98	14
Smoothtex nickel screen		(300 mesh)			0.16	174
Glass		32 × 28		0.03	1.60	17
Dacron		60 × 40	5.8		0.84	33
Dacron		76 × 48	13.4		0.29	9.5
Teflon		76 × 70	8.7		1.39	20

*Estimates based on microscopic examination.
†Measured with atmospheric air. This value will be constant only for streamline flow, which is the case for values of $\rho V_f/\mu$ of less than approximately 100.

$$K_F = \Delta p_i/\mu V_f$$

where Δp_i = pressure drop, in water; μ = gas viscosity, cP; V_f = superficial gas velocity through cloth, ft/min; and ρ = gas density, lb/ft^3.
‡Cloth, similar to previous one, that had been in service and contained dust in pores although free of surface accumulation.
§Data from Pring, *Air Pollution,* McGraw-Hill, New York, 1952, p. 280.

TABLE 17-7 Physical Properties of Selected Felts for Reverse-Pulse Filters

Fiber	Weight, oz/yd^2	Thickness, in	Breaking strength, lbf/in width	Elongation, % to rupture	Air permeability, (ft^3/min)/ft^2 at Δp_i = ½ in water	K_F
Wool	23.1	0.135			27.1	1.03
Wool	21.2	0.129			29.8	0.93
Orlon*	10.9	0.045	65	18	20–25	1.11–1.39
Orlon*	17.9	0.088	85	18	15–20	1.39–1.85
Orlon*	24	0.125	110	60	10–20	1.39–2.78
Acrilan*	17.9	0.075	100	22	15–20	1.39–1.85
Dynel*	24	0.125	60	80	30–40	0.70–0.93
Dacron*	17.9	0.080	125	22	15–20	1.39–1.85
Dacron*	9.9	0.250	20	150	200–225	0.11–0.14
Dacron*	24	0.125	175	80	20–30	0.93–1.39
Nylon*	24	0.125	100	100	30–40	0.70–0.93
Arnel*	24	0.125	60	80	30–40	0.70–0.93
Teflon	15.6	0.053			82.5	0.34
Teflon	43.5	0.119			21.6	1.29

*These data courtesy of American Felt Co.

field and laboratory studies have indicated that during the rest of the filtration cycle the effluent-dust concentration tends to remain constant regardless of the inlet concentration [Dennis, *J. Air Pollut. Control Assoc.*, **24,** 1156 (1974)]. In addition, there has been little indication that the penetration is strongly related to dust-particle size, except possibly in the low-submicrometer range. These observations appear to be generally consistent with sieving being the principal collection mechanism.

Leith and First [*J. Air Pollut. Control Assoc.*, **27,** 534 (1977); **27,** 754 (1977)] studied the collection efficiency of reverse-pulse filters and concluded that once the dust cake has been established, "straight-through" penetration by dust particles that pass through the filter without being stopped is negligible by comparison with penetration by dust that actually deposits initially and then "seeps" through the fabric to be reentrained into the exit air stream. They also noted that "pinholes" may form in the dust cake, particularly over pores between yarns in a woven fabric, and that particles may subsequently penetrate straight through at the pinholes. The formation of pinholes, or "cake puncture," had been observed earlier by Stephan et al. [*Am. Ind. Hyg. Assoc. J.*, **21,** 1 (1960)], but without measurement of the associated loss of collection efficiency. When a supported flat filter medium with extremely fine pores (e.g., glass-fiber paper, membrane filter) was used, no cake puncture took place even with very high pressure differentials across the cake. However, puncture did occur when a cotton-sateen filter fabric was used as the cake support. The formation of pinholes with certain combinations of dusts, fabrics, and filtration conditions was also observed by Koscianowski et al. (EPA-600/7-78-056, 1978). Evidently puncture occurs when the local cake structure is not strong enough to maintain a bridge over the aperture represented by a large pore and the portion of the cake covering the pore is blown through the fabric. This suggests that formation of pinholes will be highly dependent on the strength of the surface forces between particles that produce flocculation of dusts. The seepage of a dust through a filter is probably also closely related to the strength of the surface forces.

Surface pores can be greatly reduced in size by coating what will become the dusty side of the filter fabric with a thin microporous membrane that is supported by the underlying fabric. That has the effect of decreasing the effective penetration, both by eliminating cake pinholes, and by preventing the seepage of dust that is dragged through the fabric by successive cleanings. A variety of different membrane-forming polymers can be used in compatible service. The most versatile and effective surface filtration membranes are microfibrous Teflon as already described by Brinckman and Maresca [ASME Med. Waste Symp. (1992)] in the section on dry scrubbing.

Granular-Bed Filters Granular-bed filters may be classified as "depth" filters, since dust particles deposit in depth within the bed of granules. The granules themselves present targets for the deposition of particles by inertia, diffusion, flow-line interception, gravity, and electrostatic attraction, depending on the dust and filter characteristics and the operating conditions. Other deposition mechanisms are minor at most. Although it is physically possible under some circumstances for a dust layer to form on the inlet face of the filter, the practical limits of gas pressure drop will normally have been reached long before a surface dust layer can be established.

Granular-bed filters may be divided into three classes:

1. *Fixed-bed, or packed-bed, filters.* These units are not cleaned when they become plugged with deposited dust particles but are broken up for disposal or simply abandoned. If they are constructed from fine granules (e.g., sand particles), they may be designed to give high collection efficiencies on fine dust particles. However, if such a filter is to have a reasonable operating life, it can be used only on a gas containing a low concentration of dust particles.

2. *Cleanable granular-bed filters.* In these devices provisions are made to separate the collected dust from the granules either continuously or periodically, so that the units can operate continuously on gases containing moderate to high dust concentrations. The necessity for cleaning and recycling the granules generally restricts the practical lower granule size to about 3 to 10 mm. This in turn makes it difficult to attain high collection efficiencies on fine particles with granule beds of reasonable depth and gas pressure drop.

3. *Fluidized-bed filters.* Fluidized beds of granules have received considerable study on theoretical and experimental levels but have not been applied on a practical commercial scale.

Fixed Granular-Bed Filters Fixed-bed filters composed of granules have received considerable theoretical and experimental study [Thomas and Yoder, *AMA Arch. Ind. Health,* **13,** 545 (1956); **13,** 550 (1956); Knettig and Beeckmans, *Can. J. Chem. Eng.*, **52,** 703 (1974); Schmidt et al., *J. Air Pollut. Control Assoc.*, **28,** 143 (1978); Tardos et al., *J. Air Pollut. Control Assoc.*, **28,** 354 (1978); and Gutfinger and Tardos, *Atmos. Environ.,* **13,** 853 (1979)]. The theoretical approach is the same as that used in the treatment of deep-bed fibrous filters.

Fibers for filter applications can be produced with diameters smaller than it is practical to obtain with granules. Consequently, most concern with filtration of fine particles has been focused on fibrous-bed rather than granular-bed filters. However, for certain specialized applications granular beds have shown some superior properties, such as greater dimensional stability. Granular-bed filters of special design (deep-bed sand filters) have been used since 1948 for removing radioactive particles from waste air and gas streams in atomic energy plants (Lapple, "Interim Report—200 Area Stack Contamination," U.S. AEC Rep. HDC-743, Oct. 11, 1948; Juvinall et al., "Sand-Bed Filtration of Aerosols: A Review of Published Information," U.S. AEC Rep. ANL-7683, 1970; and Burchsted et al., *Nuclear Air Cleaning Handbook,* U.S. ERDA 76-21, 1976). The filter characteristics needed included high collection efficiency on fine particles, large dust-holding capacity to give long operating life, and low maintenance requirements. The sand filters are as much as 2.7 m (9 ft) in depth and are constructed in graded layers with about a 2:1 variation in the granule size from one layer to the next. The air-flow direction is upward, and the granules decrease in size in the direction of the air flow. The bottom layer is composed of rocks about 5 to 7.5 cm (2 to 3 in) in diameter, and granule sizes in successive layers decrease to 0.3 to 0.6 mm (50 to 30 mesh) in the finest layer. With superficial face velocities of about 1.5 m/min (5 ft/min), gas pressure drops of clean filters have ranged from 1.7 to 2.8 kPa (7 to 11 in water). Collection efficiencies of up to 99.98 percent with a polydisperse dioctyl phthalate aerosol of 0.7-μm mean diameter have been reported (Juvinall et al., op. cit.). Operating lives of 5 years or more have been attained.

Cleanable Granular-Bed Filters The principal objective in the development of cleanable granular-bed filters is to produce a device that can operate at temperatures above the range that can be tolerated with fabric filters. In some of the devices, the granules are circulated continuously through the unit, then are cleaned of the collected dust and returned to the filter bed. In others, the granular bed remains in place but is periodically taken out of service and cleaned by some means, such as backflushing with air.

A number of moving-bed granular filters have used cross-flow designs. One form of cross-flow moving-granular-bed filter, produced by the Combustion Power Company (Fig. 17-61), is currently in commercial use in some applications. The granular filter medium consists of ⅛- to ¼-in (3- to 6-mm) pea gravel. Gas face velocities range from 30 to 46 m/min (100 to 150 ft/min), and reported gas pressure drops are in the range of 0.5 to 3 kPa (2 to 12 in water). The original form of the device [Reese, TAPPI, **60**(3), 109 (1977)] did not incorporate electrical augmentation. Collection efficiencies for submicrometer particles were low, and the electrical augmentation was added to correct the deficiency (Parquet, "The Electroscrubber Filter: Applications and Particulate Collection Performance," EPA-600/9-82-005c, 1982, p. 363). The electrostatic grid immersed in the bed of granules is charged to a potential of 20,000 to 30,000 V, producing an electric field between the grid and the inlet and outlet louvers that enclose the bed. No ionizing electrode is used to charge particles in the incoming gas; reliance is placed on the existence of natural charges on the dust particles. Individual dust particles commonly carry positive or negative charges even though the net charge on the dust as a whole is normally neutral. Depending on their charges, dust particles are attracted or repelled by the electrical field and are therefore caused to deposit on the rocks in the bed.

Self et al. ("Electrical Augmentation of Granular Bed Filters," EPA-600/9-80-039c, 1980, p. 309) demonstrated in theoretical studies and

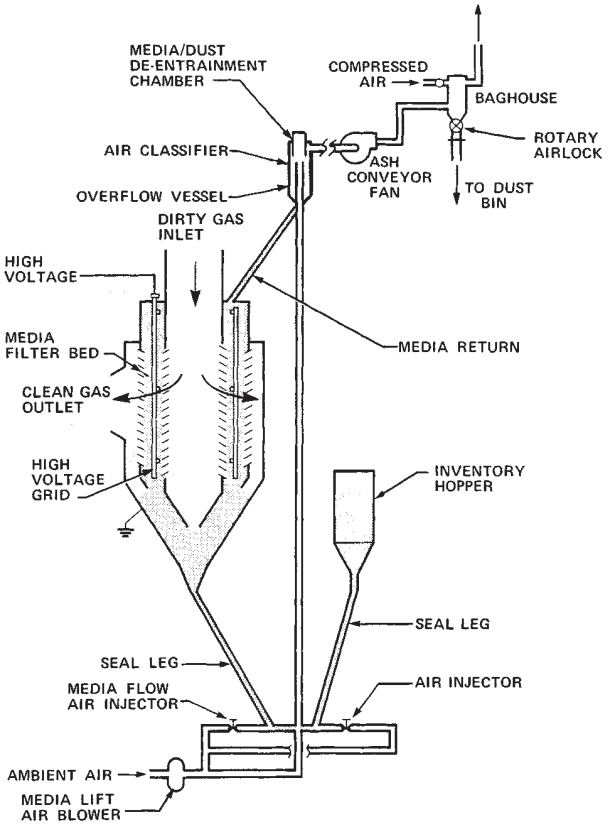


FIG. 17-61 Electrically augmented granular-bed filter. (*Combustion Power Company.*)

laboratory experiments that such an augmentation system should yield substantial increases in the collection efficiency for fine particles if the particles carry significant charges. Significant improvements in the performance of the Combustion Power units with electrical augmentation have been reported by the manufacturer (Parquet, op. cit.).

Another type of gravel-bed filter, developed by GFE in Germany, has had limited commercial application in the United States [Schueler, *Rock Prod.*, **76**(7), 66 (1973); **77**(11), 39 (1974)]. After precleaning in a cyclone, the gas flows downward through a stationary horizontal filter bed of gravel. When the bed becomes loaded with dust, the gas flow is cut off, and the bed is backflushed with air while being stirred with a double-armed rake that is rotated by a gear motor. The backflush air also flows backward through the cyclone, which then acts as a dropout chamber. Multiple filter units are constructed in parallel so that individual units can be taken off the line for cleaning. The dust dislodged from the bed and carried by the backflush air is flocculated, and part is collected in the cyclone. The backflush air with the remaining suspended dust is cleaned in the other gravel-bed filter units that are operating on line. Performance tests made on one installation for the U.S. Environmental Protection Agency (EPA-600/7-78-093, 1978) did not give clear results but indicated that collection efficiencies were low on particles under 2 μm and that some of the dust in the backflush air was redispersed sufficiently to penetrate the operating filter units.

Air Filters The types of equipment previously described are intended primarily for the collection of process dusts, whereas air filters comprise a variety of filtration devices designed for the collection of particulate matter at low concentrations, usually atmospheric dust. The difference in the two categories of equipment is not in the principles of operation but in the adaptations required to deal with the different quantities of dust. Process-dust concentrations may run as high as several hundred grams per cubic meter (or grains per cubic foot) but usually do not exceed 45 g/m^3 (20 gr/ft^3). Atmospheric-dust concentrations that may be expected in various types of locations are shown in Table 17-8 and are generally below 12 mg/m^3 (5 gr/1000 ft^3).

TABLE 17-8 Average Atmospheric-Dust Concentrations*
1 gr/1000 ft^3 = 2.3 mg/m^3

Location	Dust concentration, gr/1000 ft^3
Rural and suburban districts	0.02–0.2
Metropolitan districts	0.04–0.4
Industrial districts	0.1–2.0
Ordinary factories or workrooms	0.2–4.0
Excessive dusty factories or mines	4.0–400

**Heating Ventilating Air Conditioning Guide*, American Society of Heating, Refrigerating and Air-Conditioning Engineers, New York, 1960, p. 77.

The most frequent application of air filters is in cleaning atmospheric air for building ventilation, which usually requires only moderately high collection-efficiency levels. However, a variety of industrial operations developed mostly since the 1940s require air of extreme cleanliness, sometimes for pressurizing enclosures such as clean rooms and sometimes for use in a process itself. Examples of applications include the manufacture of antibiotics and other pharmaceuticals, the production of photographic film, and the manufacture and assembly of semiconductors and other electronic devices. Air cleaning at the necessary efficiency levels is accomplished by the use of high-efficiency fibrous filters that have been developed since the 1940s.

Air filters are also used to protect internal-combustion engines and gas turbines by cleaning the intake air. In some locations and applications, the atmospheric-dust concentrations encountered are much higher than those normally encountered in air-conditioning service.

High-efficiency air filters are sometimes used for emission control when particulate contaminants are low in concentration but present special hazards; cleaning of ventilation air and other gas streams exhausted from nuclear plant operations is an example.

Air-Filtration Theory Current high-efficiency air- and gas-filtration methods and equipment have resulted largely from the development of filtration theory since about 1930 and particularly since the 1940s. Much of the theoretical advance was originally encouraged by the requirements of the military and atomic energy programs. The fibrous filter has served both as a practical device and as a model for theoretical and experimental investigation. Extensive reviews and new treatments of air-filtration theory and experience have been presented by Chen [*Chem. Rev.*, **55,** 595 (1955)], Dorman ("Filtration," in Davies, *Aerosol Science*, Academic, New York, 1966), Pich (*Theory of Aerosol Filtration by Fibrous and Membrane Filters*, in ibid.), Davies (*Air Filtration*, Academic, New York, 1973), and Kirsch and Stechkina ("The Theory of Aerosol Filtration with Fibrous Filters," in Shaw, *Fundamentals of Aerosol Science*, Wiley, New York, 1978). The theoretical treatment of filtration starts with the processes of dust-particle deposition on collecting bodies, as outlined in Fig. 17-35 and Table 17-2. All the mechanisms shown in Table 17-2 may come into play, but inertial deposition, flow-line interception, and diffusional deposition are usually dominant. Electrostatic precipitation may become a major mechanism if the collecting body, the dust particle, or both, are charged. Gravitational settling is a minor influence for particles in the size range of usual interest. Thermal precipitation is nil in the absence of significant temperature gradients. Sieving is a possible mechanism only when the pores in the filter medium are smaller than or approximately equal to the particle size and will not be encountered in fibrous filters unless they are loaded sufficiently for a surface dust layer to form.

The theoretical prediction of the efficiency of collection of dust particles by a fibrous filter consists of three steps (Chen, op. cit.):

1. Calculation of the target efficiency η_o of an isolated fiber in an air stream having a superficial velocity the same as that in the filter
2. Determining the difference between the target efficiency of the isolated fiber and that of an individual fiber in the filter array η_t

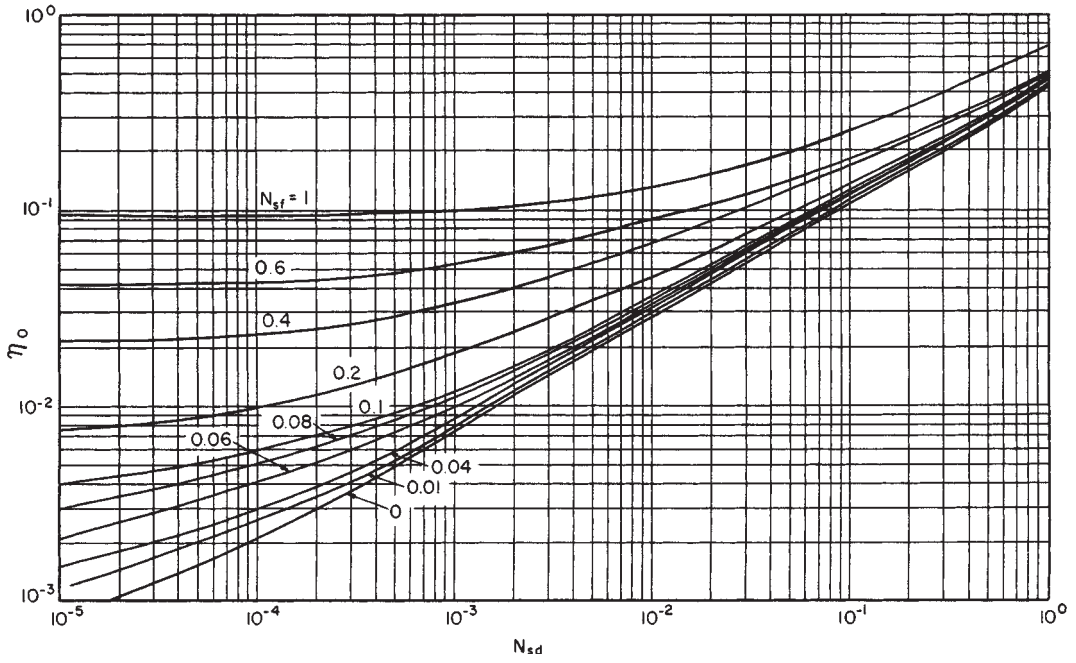


FIG. 17-62 Isolated fiber efficiency for combined diffusion and interception mechanism at $N_{Re} = 10^{-2}$. [*Chen,* Chem. Rev., ***55,*** *595 (1955).*]

3. Determining the collection efficiency of the filter η from the target efficiency of the individual fibers

The results of computations of η_o for an isolated fiber are illustrated in Figs. 17-62 and 17-63. The target efficiency η_t of an individual fiber in a filter differs from η_o for two main reasons (Pich, op. cit.): (1) the average gas velocity is higher in the filter, and (2) the velocity field around the individual fibers is influenced by the proximity of neighboring fibers. The interference effect is difficult to determine on a purely theoretical basis and is usually evaluated experimentally. Chen (op. cit.) expressed the effect with an empirical equation:

$$\eta_t = \eta_o[1 + K_\alpha(1 - \varepsilon_v)] \tag{17-14}$$

This indicates that the target efficiency of the fiber is increased by the proximity of other fibers. The value of K_α averaged 4.5 for values of the void fraction ε_v, ranging from 0.90 to 0.99. Extending use of the equation to values of ε_v lower than 0.90 may result in large errors.

The collection efficiency of the filter may be calculated from the fiber target efficiency and other physical characteristics of the filter (Chen, op. cit.):

$$N_t = \frac{4\eta_t L(1 - \varepsilon_v)}{\pi D_b \varepsilon_v} \tag{17-15}$$

where D_b = fiber diameter and L = filter thickness. The derivation of Eq. (17-15) assumes that (1) η_t is the same throughout the filter, (2) all fibers are of the same diameter D_b, are cylindrical and are normal to the direction of the gas flow, (3) the fraction of the particles deposited in any one layer of fiber is small, and (4) the gas passing through the filter is essentially completely remixed after it leaves one layer of the filter and before it enters the next. The first assumption requires that Eq. (17-15) apply only for particles of a single size for which there are corresponding values of η_t, η, and N_t.

For filters of high porosity, ε_v approaches unity and Eq. (17-15) reduces to the expression used by Wong et al. [*J. Appl. Phys.*, **27,** 161 (1956)] and Thomas and Lapple [*Am. Inst. Chem. Eng. J.*, **7,** 203 (1961)]:

$$N_t = \frac{4\eta_t L(1 - \varepsilon_v)}{\pi D_b} \tag{17-16}$$

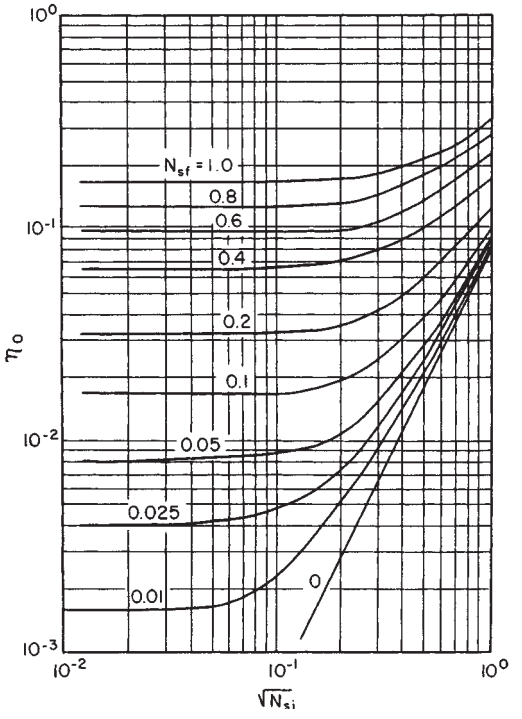


FIG. 17-63 Isolated fiber efficiency for combined inertia and interception mechanisms at $N_{Re} = 0.2$. [*Chen,* Chem. Rev., ***55,*** *595 (1955).*]

The foregoing procedure is commonly employed in reverse to determine or confirm fiber target efficiencies from the experimentally determined efficiencies of fibrous filter pads.

Filtration theory assumes that a dust particle that touches a collector body adheres to it. This assumption appears to be valid in most cases, but evidence of nonadherence, or particle bouncing, has appeared in some instances. Wright et al. ("High Velocity Air Filters," WADC TR 55-457, ASTIA Doc. AD-142075, 1957) investigated the performance of fibrous filters at filtration velocities of 0.091 to 3.05 m/s (0.3 to 10 ft/s), using 0.3-μm and 1.4-μm supercooled liquid aerosols and a 1.2-μm solid aerosol. The collection efficiencies agreed well with theoretical predictions for the liquid aerosols and apparently also for the solid aerosol at filtration velocities under 0.3 m/s (1 ft/s). But at filtration velocities above 0.3 m/s some of the solid particles failed to adhere. With a filter composed of 30-μm glass fibers and a filtration velocity of 9.1 m/s (30 ft/s), there were indications that 90 percent of the solid aerosol particles striking a fiber bounced off.

Bouncing may be regarded as a defect in the particle-deposition process. However, particles that have been deposited in filters may subsequently be blown off and reentrained into the air stream (Corn, "Adhesion of Particles," in Davies, *Aerosol Science,* Academic, New York, 1966; and Davies, op. cit.).

The theories of filtration by a fibrous filter relate only to the initial efficiency of the clean filter in the "static" period of filtration before the deposition of any appreciable quantity of dust particles. The deposition of particles in a filter increases the number of targets available to intercept particles, so that collection efficiency increases as the filter loads. At the same time, the filter undergoes clogging and the pressure drop increases. No theory is available for dealing with the "dynamic" period of filtration in which collection efficiency and pressure drop vary with the loading of collected dust. The theoretical treatment of this filtration period is incomparably more complex than that for the "static" period. Investigators have noted that both the increase in collection efficiency and the increase in pressure drop are exponential functions of the loading of collected dust or are at least roughly so (Davies, op. cit.). Some empirical relationships have been derived for correlating data in particular instances.

The dust particles collected by a fibrous filter do not deposit in uniform layers on fibers but tend to deposit preferentially on previously deposited particles (Billings, "Effect of Particle Accumulation in Aerosol Filtration," Ph.D. dissertation, California Institute of Technology, Pasadena, 1966), forming chainlike agglomerates termed "dendrites." The growth of dendritic deposits on fibers has been studied experimentally [Billings, op. cit.; Bhutra and Payatakes, *J. Aerosol Sci.,* **10,** 445 (1979)], and Payatakes and coworkers [Payatakes and Tien, *J. Aerosol Sci.,* **7,** 85 (1976); Payatakes, *Am. Inst. Chem. Eng. J.,* **23,** 192 (1977); and Payatakes and Gradon, *Chem. Eng. Sci.,* **35,** 1083 (1980)] have attempted to model the growth of dendrites and its influence on filter efficiency and pressure drop.

Air-Filter Types Air filters may be broadly divided into two classes: (1) panel, or unit, filters; and (2) automatic, or continuous, filters. Panel filters are constructed in units of convenient size (commonly 20- by 20-in or 24- by 24-in face area) to facilitate installation, maintenance, and cleaning. Each unit consists of a cleanable or replaceable cell or filter pad in a substantial frame that may be bolted to the frames of similar units to form an airtight partition between the source of the dusty air and the destination of the cleaned air.

Panel filters may use either viscous or dry filter media. Viscous filters are so called because the filter medium is coated with a tacky liquid of high viscosity (e.g., mineral oil and adhesives) to retain the dust. The filter pad consists of an assembly of coarse fibers (now usually metal, glass, or plastic). Because the fibers are coarse and the media are highly porous, resistance to air flow is low and high filtration velocities can be used.

Dry filters are usually deeper than viscous filters. The dry filter media use finer fibers and have much smaller pores than the viscous media and need not rely on an oil coating to retain collected dust. Because of their greater resistance to air flow, dry filters must use lower filtration velocities to avoid excessive pressure drops. Hence, dry media must have larger surface areas and are usually pleated or arranged in the form of pockets (Fig. 17-64), generally sheets of cellulose pulp, cotton, felt, or spun glass.

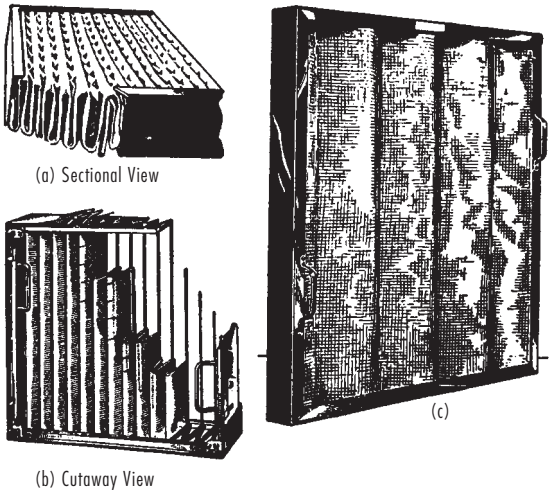


FIG. 17-64 Typical dry filters. (*a*) Throwaway type, Airplex. (*Davies Air Filter Corporation.*) (*b*) Replaceable medium type, Airmat PL-24, cutaway view. (*American Air Filter Co., Inc.*) (*c*) Cleanable type, Amirglass sawtooth. (*Amirton Company.*)

Automatic filters are made with either viscous-coated or dry filter media. However, the cleaning or disposal of the loaded medium is essentially continuous and automatic. In most such devices the air passes horizontally through a movable filter curtain. As the filter loads with dust, the curtain is continuously or intermittently advanced to expose clean media to the air flow and to clean or dispose of the loaded medium. Movement of the curtain can be provided by a hand crank or a motor drive. Movement of a motor-driven curtain can be actuated automatically by a differential-pressure switch connected across the filter.

High-Efficiency Air Cleaning Air-filter systems for nuclear facilities and for other applications demanding extremely high standards of air purity require filtration efficiencies well beyond those attainable with the equipment described above. The *Nuclear Air Cleaning Handbook* (Burchsted et al., op. cit.) presents an extensive treatment of the requirements for and the design of such air-cleaning facilities. Much of the material is pertinent to high-efficiency air-filter systems for applications to other than nuclear facilities.

HEPA (high-efficiency particulate air) filters were originally developed for nuclear and military applications but are now widely used and are manufactured by numerous companies. By definition, an HEPA filter is a "throwaway, extended-medium dry-type" filter having (1) a minimum particle-removal efficiency of not less than 99.97 percent for 0.3-μm particles, (2) a maximum resistance, when clean, of 1.0 in water when operated at rated air-flow capacity, and (3) a rigid casing extending the full depth of the medium (Burchsted et al., op. cit.). The filter medium is a paper made of submicrometer glass fibers in a matrix of larger-diameter (1- to 4-μm) glass fibers. An organic binder is added during the papermaking process to hold the fibers and give the paper added tensile strength. Filter units are made in several standard sizes (Table 17-9).

TABLE 17-9 Standard HEPA Filters*

Face dimensions, in	Depth, less gaskets, in	Design air-flow capacity at clean-filter resistance of 1.0 in water (standard ft³/min)
24 × 24	11½	1000
24 × 24	5⅞	500
12 × 12	5⅞	125
8 × 8	5⅞	20
8 × 8	3⅛	25

*Burchsted et al., *Nuclear Air Cleaning Handbook,* ERDA 76-21, Oak Ridge, Tenn., 1976.

Because HEPA filters are designed primarily for high efficiency, their dust-loading capacities are limited, and it is common practice to use prefilters to extend their operating lives. In general, HEPA filters should be protected from (1) lint, (2) particles larger than 1 to 2 μm in diameter, and (3) dust concentrations greater than 23 mg/m^3 (10 gr/1000 ft^3). Air filters used in nuclear facilities as prefilters and building-supply air filters are classified as shown in Table 17-10. The standard of the American Society of Heating, Refrigerating and Air-Conditioning Engineers (*Method of Testing Air Cleaning Devices Used in General Ventilation for Removing Particulate Matter,* ASHRAE 52-68, 1968) requires both a dust-spot (dust-stain) efficiency test made with atmospheric dust and a weight-arrestance test made with a synthetic test dust. A more precise comparison of the different groups of filters, based on removal efficiencies for particles of specific sizes, is presented in Table 17-11.

Table 17-12 presents the relative performance of Group I, II, and III filters with respect to air-flow capacity, resistance, and dust-holding capacity. The dust-holding capacities correspond to the manufacturers' recommended maximum allowable increases in air-flow resistance. The values for dust-holding capacity are based on tests with a synthetic dust and hence are relative. The actual dust-holding capacity in a specific application will depend on the characteristics of the dust encountered. In some instances it may be appropriate to use two or more stages of precleaning in air-filter systems to achieve a desired combination of operating life and efficiency. In very dusty locations, inertial devices such as multiple small cyclones may be used as first-stage separators.

Electrical Precipitators When particles suspended in a gas are exposed to gas ions in an electrostatic field, they will become charged and migrate under the action of the field. The functional mechanisms of electrical precipitation may be listed as follows:

1. Gas ionization
2. Particle collection
   - *a.* Production of electrostatic field to cause charging and migration of dust particles
   - *b.* Gas retention to permit particle migration to a collection surface
   - *c.* Prevention of reentrainment of collected particles
   - *d.* Removal of collected particles from the equipment

TABLE 17-10 Classification of Common Air Filters*

Group	Efficiency	Filter type	Stain test efficiency, %	Arrestance, %
I	Low	Viscous impingement, panel type	<20†	40–80†
II	Moderate	Extended medium, dry type	20–60†	80–96†
III	High	Extended medium, dry type	60–98‡	96–99†
HEPA	Extreme	Extended medium, dry type	100§	100†

*Burchsted et al., *Nuclear Air Cleaning Handbook,* ERDA 76-21, Oak Ridge, Tenn., 1976.
†Test using synthetic dust.
‡Stain test using atmospheric dust.
§ASHRAE/52-68, American Society of Heating, Refrigerating and Air-Conditioning Engineers.

TABLE 17-11 Comparison of Air Filters by Percent Removal Efficiency for Various Particle Sizes*

Group	Efficiency	Removal efficiency, %, for particle size of 0.3 μm	1.0 μm	5.0 μm	10.0 μm
I	Low	0–2	10–30	40–70	90–98
II	Moderate	10–40	40–70	85–95	98–99
III	High	45–85	75–99	99–99.9	99.9
HEPA	Extreme	99.97 min	99.99	100	100

*Burchsted et al., *Nuclear Air Cleaning Handbook,* ERDA 76-21, Oak Ridge, Tenn., 1976.

TABLE 17-12 Air-Flow Capacity, Resistance, and Dust-Holding Capacity of Air Filters*

Group	Efficiency	Air-flow capacity, ft^3/(min·ft^2 of frontal area)	Resistance, in water: Clean filter	Resistance, in water: Used filter	Dust-holding capacity, g/(1000 ft^3·min of air-flow capacity)
I	Low	300–500	0.05–0.1	0.3–0.5	50–1000
II	Moderate	250–750	0.1–0.5	0.5–1.0	100–500
III	High	250–750	0.20–0.5	0.6–1.4	50–200

*Burchsted et al., *Nuclear Air Cleaning Handbook,* ERDA 76-21, Oak Ridge, Tenn., 1976.

There are two general classes of electrical precipitators: (1) single-stage, in which ionization and collection are combined; (2) two-stage, in which ionization is achieved in one portion of the equipment, followed by collection in another. Various types in each class differ essentially in the details by which each function is accomplished.

The underlying theory presented in the following paragraphs assumes that the dust concentration is small, since only very incomplete evaluations for conditions of high dust concentration have been made.

Field Strength Whereas the applied potential or voltage is the quantity commonly known, it is the field strength that determines behavior in an electrostatic field. When the current flow is low (i.e., before the onset of spark or corona discharge), these are related by the following equations for two common forms of electrodes:

Parallel plates:

$$\mathscr{E} = E/B_e \tag{17-17}$$

Concentric cylinders (wire-in-cylinder):

$$\mathscr{E} = \frac{E}{r \ln (D_t/D_d)} \tag{17-18}$$

The field strength is uniform between parallel plates, whereas it varies in the space between concentric cylinders, being highest at the surface of the central cylinder. After corona sets in, the current flow will become appreciable. The field strength near the center electrode will be less than given by Eq. (17-18) and that in the major portion of the clearance space will be greater and more uniform [see Eqs. (17-23) and (17-24)].

Potential and Ionization In order to obtain gas ionization it is necessary to exceed, at least locally, the electrical breakdown strength of the gas. Corona is the name applied to such a local discharge that fails to propagate itself. Sparking is essentially an advanced stage of corona in which complete breakdown of the gas occurs along a given path. Since corona represents a local breakdown, it can occur only in a nonuniform electrical field (Whitehead, *Dielectric Phenomena—Electrical Discharge in Gases,* Van Nostrand, Princeton, N.J., 1927, p. 40). Consequently, for parallel plates, only sparking occurs at a field strength or potential difference given by the empirical expressions

$$\mathscr{E}_s = \mathscr{E}_o k_\rho \left[1 + \left(\frac{K_o}{k_\rho B_e}\right)\right] \tag{17-19}$$

$$E_s = \mathscr{E}_o k_\rho B_e + K_o \mathscr{E}_o \tag{17-20}$$

For air in the range of $k_\rho B_e$ from 0.1 to 2, $\mathscr{E}_o = 111.2$ and $K_o = 0.048$. Thornton [*Phil. Mag.,* **28**(7), 666 (1939)] gives values for other gases. For concentric cylinders (Loeb, *Fundamental Processes of Electrical Discharge in Gases,* Wiley, New York, 1939; Peek, *Dielectric Phenomena in High-Voltage Engineering,* McGraw-Hill, New York, 1929; and Whitehead, op. cit.), corona sets in at the central wire when

$$\mathscr{E}_c = \mathscr{E}_o k_\rho \left(1 + \sqrt{\frac{K_o}{k_\rho D_d}}\right) \tag{17-21}$$

$$E_c = \left(\frac{\mathscr{E}_o k_\rho D_d}{2}\right)\left(1 + \sqrt{\frac{K_o}{k_\rho D_d}}\right) \ln \left(\frac{D_t}{D_d}\right) \tag{17-22}$$

TABLE 17-13 Sparking Potentials* (Small Wire Concentric in Pipe)

Pipe diameter, in	Sparking potential,† volts	
	Peak	Root mean square
4	59,000	45,000
6	76,000	58,000
9	90,000	69,000
12	100,000	77,000

*Data reported by Anderson in Perry, "Chemical Engineers' Handbook," 2d ed., p. 1873, McGraw-Hill, New York, 1941.

†For gases at atmospheric pressure, 100°F, containing water vapor, air, CO_2, and mist, and negative-discharge-electrode polarity.

For air approximate values are $\mathscr{E}_o = 110$, $K_o = 0.18$. Corona, however, will set in only if $(D_t/D_d) > 2.718$. If this ratio is less than 2.718, no corona occurs, and only sparking will result, following the laws given by Eqs. (17-21) and (17-22) (Peek, op. cit.).

In practice, precipitators are usually operated at the highest voltage practicable without sparking, since this increases both the particle charge and the electrical precipitating field. The sparking potential is generally higher with a negative charge on the discharge electrode and is less erratic in behavior than a positive corona discharge. It is the consensus, however, that ozone formation with a positive discharge is considerably less than with a negative discharge. For these reasons negative discharge is generally used in industrial precipitators, and a positive discharge is utilized in air-conditioning applications. In Table 17-13 are given some typical values for the sparking potential for the case of small wires in pipes of various sizes. The sparking potential varies approximately directly as the density of the gas but is very sensitive to the character of any material collected on the electrodes. Even small amounts of poorly conducting material on the electrodes may markedly lower the sparking voltage. For positive polarity of the discharge electrode, the sparking voltage will be very much lower. The sparking voltage is greatly affected by the temperature and humidity of the gas, as shown in Fig. 17-65.

Current Flow Corona discharge is accompanied by a relatively small flow of electric current, typically 0.1 to 0.5 mA/m^2 of collecting-electrode area (projected, rather than actual area). Sparking usually involves a considerably larger flow of current which cannot be tolerated except for occasional periods of a fraction of a second duration, and then only when suitable electrical controls are provided to limit the current. However, when suitable controls are provided, precipitators have been operated continuously with a small amount of sparking

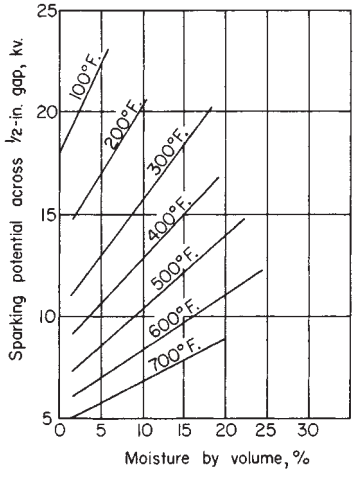


FIG. 17-65 Sparking potential for negative point-to-plane ½-in (1.3-cm) gap as a function of moisture content and temperature of air at 1-atm (101.3-kPa) pressure. [*Sproull and Nakada,* Ind. Eng. Chem., ***43,*** *1356 (1951).*]

to ensure that the voltage is in the correct range to ensure corona. Besides disruptive effects on the electrical equipment and electrodes, sparking will result in low collection efficiency because of reduction in applied voltage, redispersion of collected dust, and current channeling. Although an exact calculation can be made for the current flow for a direct-current potential applied between concentric cylinders, the following simpler expression, based on the assumption of a constant space charge or ion density, gives a good approximation of corona current [Ladenburg, *Ann. Phys.*, **4**(5), 863 (1930)]:

$$I = \frac{8\lambda_i E(E - E_c)}{D_t^2 \ln (D_t/D_d)} \tag{17-23}$$

and the average space charge is given by (Whitehead, op. cit.)

$$\sigma_{avg} = \frac{4(E - E_c)}{\pi D_t^2 \varepsilon} \tag{17-24}$$

In the space outside the immediate vicinity of corona discharge, the field strength is sensibly constant, and an average value is given by

$$\mathscr{E} = \sqrt{2I/\lambda_i} \tag{17-25}$$

which applies if the potential difference is above the critical potential required for corona discharge so that an appreciable current flows.

Ionic mobilities are given by Loeb (*International Critical Tables,* vol. 6, McGraw-Hill, New York, 1929, p. 107). For air at 0°C, 760 mmHg, $\lambda_i = 624$ (cm/s)/(statV/cm) for negative ions. Positive ions usually have a slightly lower mobility. Loeb (*Basic Processes of Gaseous Electronics,* University of California Press, Berkeley and Los Angeles, 1955, p. 53) gives a theoretical expression for ionic mobility of gases which is probably good to within ±50 percent:

$$\lambda_i = \frac{100.0}{k_p \sqrt{(\delta_g - 1)M}} \tag{17-26}$$

In general, ionic mobilities are inversely proportional to gas density. Ionic velocities in the usual electrostatic precipitator are on the order of 30.5 m/s (100 ft/s).

Electric Wind By virtue of the momentum transfer from gas ions moving in the electrical field to the surrounding gas molecules, a gas circulation, known as the "electric" or "ionic" wind, is set up between the electrodes. For conditions encountered in electrical precipitators, the velocity of this circulation is on the order of 0.6 m/s (2 ft/s). Also, as a result of this momentum transfer, the pressure at the collecting electrode is slightly higher than at the discharge electrode (Whitehead, op. cit., p. 167).

Charging of Particles [Deutsch, *Ann. Phys.,* **68**(4), 335 (1922); **9**(5), 249 (1931); **10**(5), 847 (1931); Ladenburg, op. cit.; and Mierdel, *Z. Tech. Phys.,* **13,** 564 (1932).] Three forces act on a gas ion in the vicinity of a particle: attractive forces due to the field strength and the ionic image; and repulsive forces due to the Coulomb effect. For spherical particles larger than 1-μm diameter, the ionic image effect is negligible, and charging will continue until the other two forces balance according to the equation

$$N_o = \left(\frac{\zeta \mathscr{E} D_p^2}{4\varepsilon}\right)\left(\frac{\pi\sigma\varepsilon t\lambda_i}{1 + \pi\sigma\varepsilon\lambda_i t}\right) \tag{17-27}$$

The ultimate charge acquired by the particle is given by

$$N_o = \zeta \mathscr{E} D_p^2/4\varepsilon \tag{17-28}$$

and is very nearly attained in a fraction of a second. For particles smaller than 1-μm diameter, the initial charging will occur according to Eq. (17-27). However, owing to the ionic-image effect, the ultimate charge will be considerably greater because of penetration resulting from the kinetic energy of the gas ions. For charging times of the order encountered in electrical precipitation, the ultimate charge acquired by spherical particles smaller than about 1-μm diameter may be approximated (±30 percent) by the empirical expression

$$N_o = 3.4 \times 10^3 D_p T \tag{17-29}$$

Values of N_o for various sized particles are listed in Table 17-14 for 70°F, $\zeta = 2$, and $\mathscr{E} = 10$ statV/cm.

Particle Mobility By equating the electrical force acting on a

TABLE 17-14 Charge and Motion of Spherical Particles in an Electric Field

For $\zeta = 2$, and $\varepsilon = \varepsilon_i = \varepsilon_p = 10$ statV/cm

Particle diam., μ	Number of elementary electrical charges, N_0	Particle migration velocity,* u_e, ft/sec
0.1	10	0.27
.25	25	.15
.5	50	.12
1.0	105	.11
2.5	655	.26
5.0	2,620	.50
10.0	10,470	.98
25.0	65,500	2.40

NOTE: To convert feet per second to meters per second, multiply by 0.3048.

particle to the resistance due to air friction, as expressed by Stokes' law, the particle velocity or mobility may be expressed by

1. For particles larger than 1-μm diameter:

$$\lambda_p = \left(\frac{u_e}{\mathscr{E}_p}\right) = \frac{\zeta D_p \mathscr{E}_i K_m}{12\pi\mu} \tag{17-30}$$

2. For particles smaller than 1-μm diameter:

$$\lambda_p = \left(\frac{u_e}{\mathscr{E}_p}\right) = \frac{360 K_m \varepsilon T}{\mu} \tag{17-31}$$

For single-stage precipitators, $\mathscr{E}_i$ and $\mathscr{E}_p$ may be considered as essentially equal. It is apparent from Eq. (17-31) that the mobility in an electric field will be almost the same for all particles smaller than about 1-μm diameter, and hence, in the absence of reentrainment, collection efficiency should be almost independent of particle size in this range. Very small particles will actually have a greater mobility because of the Stokes-Cunningham correction factor. Values of u_e are listed in Table 17-14 for 70°F, $\zeta = 2$, and $\mathscr{E} = \mathscr{E}_i = \mathscr{E}_p = 10$ statV/cm.

Collection Efficiency Although actual particle mobilities may be considerably greater than would be calculated on the basis given in the preceding paragraph because of the action of the electric wind in single-stage precipitators, the latter acts in a compensating fashion, and the overall effect of the electric wind is probably to provide an equalization of particle concentration between the electrodes similar to the action of normal turbulence (Mierdel, op. cit.). On this basis Deutsch (op. cit.) has derived the following equations for collection efficiency, the form of which had previously been suggested by Anderson on the basis of experimental data:

$$\eta = 1 - e^{-(u_e A_e/q)} = 1 - e^{-K_e u_e} \tag{17-32}$$

For the concentric-cylinder (or wire-in-cylinder) type of precipitator, $K_e = 4L_e/D_i V_e$; for rod-curtain or wire-plate types, $K_e = L_e/B_e V_e$. Strictly speaking, Eq. (17-32) applies only for a given particle size, and the overall efficiency must be obtained by an integration process for a specific dust distribution, as described in the subsection "Cyclone Separators." However, over limited ranges of performance conditions, Eq. (17-32) has been found to give a good approximation of overall collection efficiency, with the term for particle migration velocity representing an empirical average value. Such values, calculated from overall collection-efficiency measurements, are given in Table 17-15 for specific installations.

For two-stage precipitators with close collecting-plate spacings (Figs. 20-152, 20-153), the gas flow is substantially streamline, and no electric wind exists. Consequently, with reentrainment neglected, collection efficiency may be expressed as [Penny, *Electr. Eng*, **56,** 159 (1937)]

$$\eta = u_e L_e / V_e B_e \tag{17-33}$$

which holds for values of $\eta \leqq 1.0$. In practice, however, extraneous factors may cause the actual efficiency to approach a relationship of the type given by Eq. (17-32).

Application The theoretical considerations that have been expounded should be used only for order-of-magnitude estimates, since a number of extraneous factors may enter into actual performance. In actual installations rectified alternating current is employed. Hence the electric field is not fixed but varies continuously, depending on the waveform of the rectifier, although Schmidt and Anderson [*Electr. Eng.*, **57,** 332 (1938)] report that the waveform is not a critical factor. Allowances for high dust concentrations have not been fully studied, although Deutsch (op. cit.) has presented a theoretical approach. In addition, irregularities on the discharge electrode will result in local discharges. Such irregularities can readily result from dust incrustation on the discharge electrodes due to charging of particles with opposite polarity within the thin but appreciable flow or ionization layer surrounding this electrode. Very high dust loadings increase the potential difference required for corona and reduce the current due to the space charge of the particles. This tends to reduce the average particle charge and reduces collection efficiency. This can be compensated for by increasing the potential difference when high dust loadings are involved.

TABLE 17-15 Performance Data on Typical Single-Stage Electrical Precipitator Installations*

Type of precipitator	Type of dust	Gas volume, cu ft/min	Average gas velocity, ft/sec	Collecting electrode area, sq ft	Overall collection efficiency, %	Average particle migration velocity, ft/sec
Rod curtain	Smelter fume	180,000	6	44,400	85	0.13
Tulip type	Gypsum from kiln	25,000	3.5	3,800	99.7	.64
Perforated plate	Fly ash	108,000	6	10,900	91	.40
Rod curtain	Cement	204,000	9.5	26,000	91	.31

*Research-Cottrell, Inc. To convert cubic feet per minute to cubic meters per second, multiply by 0.00047; to convert feet per second to meters per second, multiply by 0.3048; and to convert square feet to square meters, multiply by 0.0929.

Several investigators have attempted to modify the basic Deutsch equation so that it would more nearly describe precipitator performance. Cooperman ("A New Theory of Precipitator Efficiency," Pap. 69-4, APCA meeting, New York, 1969) introduced correction factors for diffusional forces arising from variations in particle concentration along the precipitator length and also perpendicular to the collecting surface. Robinson [*Atmos. Environ.* **1**(3), 193 (1967)] derived an equation for collection efficiency in which two erosion or reentrainment terms are introduced.

An analysis of precipitator performance based on theoretical considerations was undertaken by the Southern Research Institute for the National Air Pollution Control Administration (Nichols and Oglesby, "Electrostatic Precipitator Systems Analysis," AIChE annual meeting, 1970). A mathematical model was developed for calculating the particle charge, electric field, and collection efficiency based on the Deutsch-Anderson equation. The system diagram is shown in Fig. 17-66. This system-analysis method, using high-speed computers, makes it possible to analyze what takes place in each increment of precipitator length. Collection efficiency versus particle size is computed for each 1 ft (0.3 m) of gas travel, and the inlet particle-size distribution is modified accordingly. Computed overall efficiencies compare well with measured values on three precipitators. The model assumes that field charging is the only charging mechanism. The authors considered the addition of several refinements to the program: the influence of diffusion charging; reentrainment effects due to rapping and erosion; and loss of efficiency due to maldistribution of gas, dust resistivity, and gas-property effects. The modeling technique appeared promising, but much more work was needed before it could be used for design. The same authors prepared a general treatise (Oglesby and Nichols, *A Manual of Electrostatic Precipitator Technology*, parts I and II, Southern Research Institute, Birmingham, Ala., U.S. Government Publications PB196360, 196381, 1970).

High-Pressure-High-Temperature Electrostatic Precipitation In general, increased pressure increases precipitation efficiency, although a somewhat higher potential is required, because it reduces ion mobility and hence increases the potential required for corona

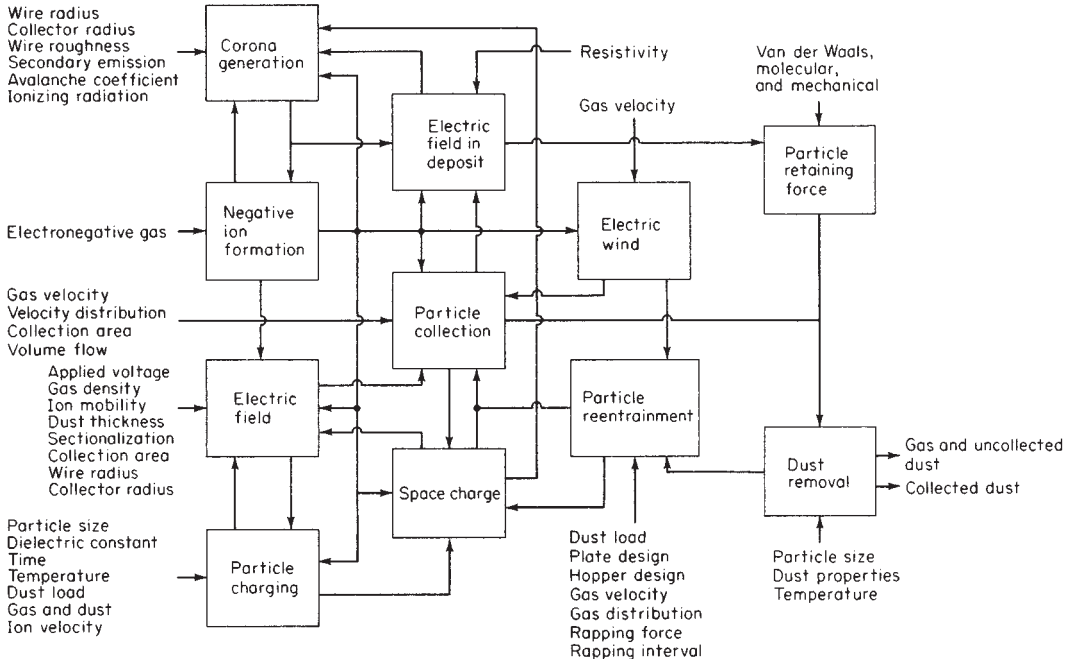


FIG. 17-66 Electrostatic-precipitator-system model. (*Nichols and Oglesby, "Electrostatic Precipitator Systems Analysis," AIChE annual meeting, 1970.*)

and sparking. Increased temperature reduces collection efficiency because ion mobility is increased, lowering critical potentials, and because gas viscosity is increased, reducing migration velocities.

Precipitators have been operated at pressures up to 5.5 MPa (800 psig) and temperatures to 800°C.

The effect of increasing gas density on sparkover voltage has been investigated by Robinson [*J. Appl. Phys.*, **40,** 5107 (1969); *Air Pollution Control,* part 1, Wiley-Interscience, New York, 1971, chap. 5]. Figure 17-67 shows the effect of gas density on corona-starting and sparkover voltages for positive and negative corona in a pipe precipitator. The sparkover voltages are experimental and are given by the solid points. Experimental corona-starting voltages are given by the hollow points. The solid lines are corona-starting voltage curves calculated from Eq. (17-33). This is an empirical relationship developed by Robinson.

$$\frac{E_c}{\rho'} = A\frac{B}{\sqrt{D_d\,\rho'/2}} \qquad (17\text{-}34)$$

E_c is the corona-starting field, kV/cm. ρ' is the relative gas density, equal to the actual gas density divided by the density of air at 25°C, 1 atm. D_d is the diameter of the ionizing wire, cm. A and B are constants which are characteristics of the gas. In dry air, $A = 32.2$ kV/cm and $B = 8.46$ kV/cm$^{1/2}$. Agreement between experimental and calculated starting voltages is good for the case of positive corona, but in the case of negative corona the calculated line serves as an upper limit for the data. This lower-than-expected starting-voltage characteristic of negative corona is confirmed by Hall et al. [*Oil Gas J.*, **66,** 109 (1968)] in a report of an electrostatic precipitator which removes lubricating-oil mist from natural gas at 5.5 MPa (800 psig) and 38°C (100°F). The use of electrostatic precipitators at elevated pressure is expected to in-

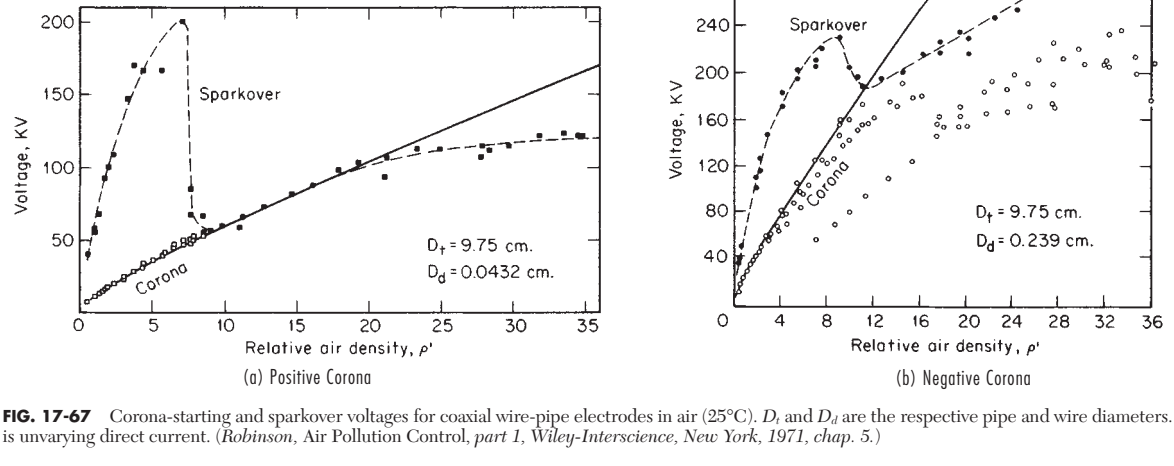


FIG. 17-67 Corona-starting and sparkover voltages for coaxial wire-pipe electrodes in air (25°C). D_t and D_d are the respective pipe and wire diameters. The voltage is unvarying direct current. (*Robinson,* Air Pollution Control, *part 1, Wiley-Interscience, New York, 1971, chap. 5.*)

crease, because the method requires very low pressure drop [approximately 69 Pa (0.1 lbf/in^2)]. This results from the fact that the electric separation forces are applied directly to the particles themselves rather than to the entire mass of the gas, as in inertial separators. The use of electrostatic precipitators at temperatures up to 400°C is well developed for the powerhouse fly-ash application, but in the range of 600 to 800°C they are still in the experimental phase. The U.S. Bureau of Mines has tested a pilot-scale tubular precipitator for fly ash. See Shale [*Air Pollut. Control Assoc. J.*, **17,** 159 (1967)] and Shale and Fasching (*Operating Characteristics of a High-Temperature Electrostatic Precipitator,* U.S. Bur. Mines Rep. 7276, 1969). It operated over a temperature range of 27 to 816°C (80 to 1500°F) and a pressure range of 552 kPa (35 to 80 psig). Initial collection efficiencies ranged from 90 to 98 percent at 793°C (1460°F), 552 kPa (80 psig), but continuous operation was not achieved because of excessive thermal expansion of internal parts.

Resistivity Problems Optimum performance of electrostatic precipitators is achieved when the electrical resistivity of the collected dust is sufficiently high to result in electrostatic pinning of the particles to the collecting surface, but not so high that dielectric breakdown of the dust layer occurs as the corona current passes through it. The optimum resistivity range is generally considered to be from 10^8 to 10^{10} Ω·cm, measured at operating conditions. As the dust builds up on the collecting electrode, it impedes the flow of current, so that a voltage drop is developed across the dust layer:

$$E_d = j\rho_d L_d \qquad (17\text{-}35)$$

If E_d/L_d exceeds the dielectric strength of the dust layer, sparks occur in the deposit and form back-corona craters. Ions of both polarities are formed. Positive ions formed in the craters are attracted to the negatively charged particles in the gas stream, whose charge level is reduced so that collection efficiency decreases. Some of the positive ions neutralize part of the negative-space-charge cloud normally present near the wire, thereby increasing total current. Collection efficiency under these conditions will not correlate with total power input (Owens, E. I. du Pont de Nemours & Co. internal communication, 1971). Under normal conditions, collection efficiency is an exponential function of corona power (White, *Industrial Electrostatic Precipitation,* Addison-Wesley, Reading, Mass., 1963). With typical ion density in the range of 10^9/cm^3, overall voltage gradient would be about 4000 V/cm, and current about 1 μA/cm^2. Dielectric breakdown of the dust layer (at about 10,000 V/cm) would therefore be expected for dusts with resistivities above 10^{10} Ω·cm.

Problems due to high resistivity are of great concern in **fly-ash** precipitation because air-pollution regulations require that coals have low (<1 percent) sulfur content. Figure 17-68 shows that the resistivity of low-sulfur coal ash exceeds the threshold of 10^{10} Ω·cm at common operating temperatures. This has resulted in the installation of a number of precipitators which have failed to meet guaranteed performance. This has occurred to an alarming extent in the United States but has also been encountered in Australia, where the sulfur content is typically 0.3 to 0.6 percent. Maartmann (Pap. EN-34F, 2d International Clean Air Congress, Washington, 1970) reports the installation of a number of precipitators which performed below guarantees, so that the Electricity Commission of New South Wales decided that each manufacturer wishing to bid on a new station must first make pilot tests to prove performance on the actual coal to be burned in that station. Problems of back corona and excessive sparking with low-sulfur coal usually require that the operating voltage be reduced. This reduces the migration velocity and leads to larger precipitators. Ramsdell (*Design Criteria for Precipitators for Modern Central Station Power Plants,* American Power Conference, Chicago, 1968) developed the curves in Fig. 17-69. They show the results of extensive field tests by the Consolidated Edison Co. In another paper ("Antipollution Program of Consolidated Edison Co. of New York," ASCE, May 13–17, 1968), Ramsdell traces the remarkable growth in the size of precipitators required for high efficiency on low-sulfur coals. The culmination of this work was the precipitator at boiler 30 at Ravenswood Station, New York. Resistivity problems were avoided by operating at high temperature [343°C (650°F)]. The mechanical

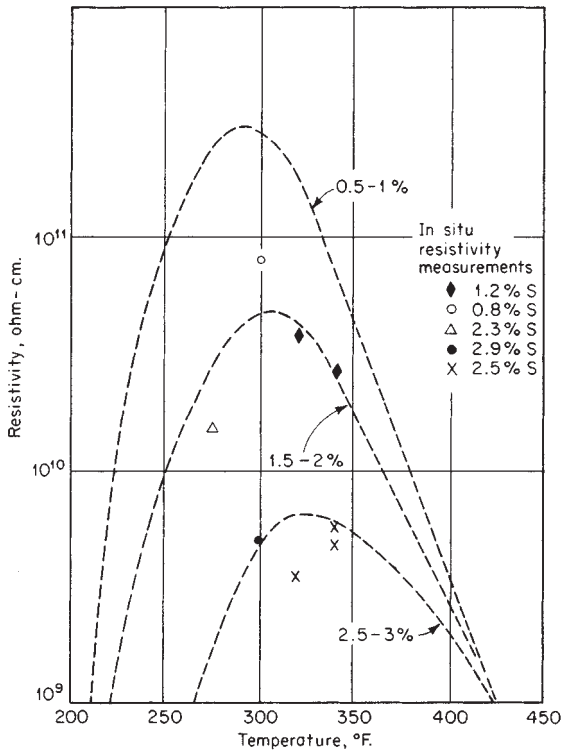


FIG. 17-68 Trends in resistivity of fly ash with variations in flue-gas temperature and coal sulfur content. °C = (°F − 32) × 5/9. (*Oglesby and Nichols,* A Manual of Electrostatic Precipitator Technology, *part II, Southern Research Institute, Birmingham, Ala., 1970.*)

(cyclone) collector was installed after the precipitator to clean up puffs due to rapping.

Maartmann (op. cit.) agrees that sulfur content is important but feels that it should not be the sole criterion for the determination of collecting surface. He points to specific collecting-surface requirements as high as 500 ft^2/(1000 ft^3·min) for 95 percent collection efficiency with high-resistivity Australian ash.

Schmidt and Anderson (op. cit.) and Anderson [*Physics,* **3,** 23 (July 1932)] claim that resistivity of the collected dust may be a controlling factor which is very sensitive to moisture. They state that an increase in relative humidity of 5 percent may double the precipitation rate because of its effect on the conductivity of the collected dust layer.

Conditioning agents have been added to the flue gas to alter dust resistivity. Steam, sodium chloride, sulfur trioxide, and ammonia have all been successfully used. Research by Chittum and others [Schmidt, *Ind. Eng. Chem.,* **41,** 2428 (1949)] led to a theory of conditioning by alteration of the moisture-adsorption properties of dust surfaces. Chittum proposed that an intermediate chemical-adsorption film, which was strongly bound to the particle and which in turn strongly adsorbed water, would be an effective conditioner. This explains how acid conditioners, such as SO_3, help resistivity problems associated with basic dusts, such as many types of fly ash, whereas ammonia is a good additive for acidic dusts such as alumina. Moisture alone can be used as a conditioning agent. This is shown in Fig. 17-65. Moisture is beneficial in two ways: it reduces the electrical resistivity of most dusts (an exception is powdered sulfur, which apparently does not absorb water), and it increases the voltage which may safely be employed without sparking, as shown in Fig. 17-65.

Low resistivity can sometimes be a problem. If the resistivity is below 10^4 Ω·cm, the collected particles are so conductive that their charges leak to ground faster than they are replenished by the corona. The particles are no longer electrostatically pinned to the plate, and

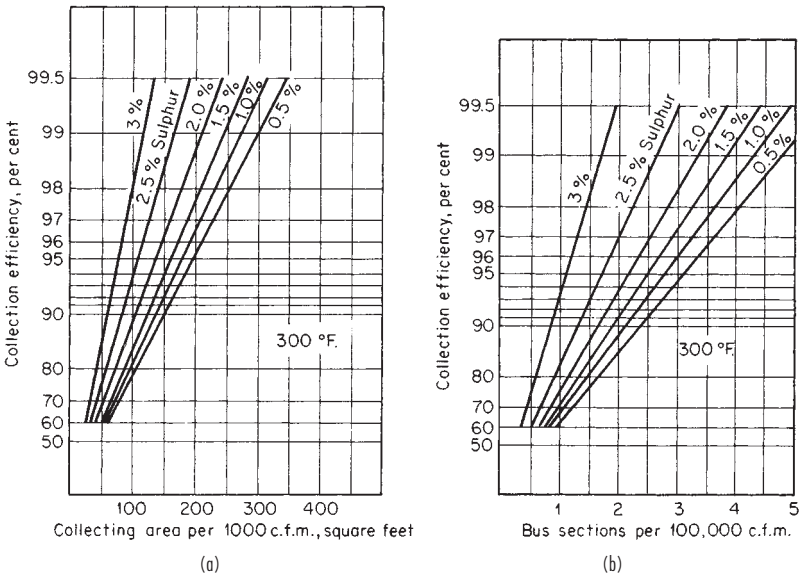


FIG. 17-69 Design curves for electrostatic precipitators for fly ash. Collection efficiency for various levels of percent sulfur in coal versus (*a*) specific collecting surface, and (*b*) bus sections per 100,000 ft^3/min (4.7 m^3/s). °C = (°F − 32) × 5/9. (*Ramsdell,* Design Criteria for Precipitators for Modern Central Station Power Plants, *American Power Conference, Chicago, Ill., 1968.*)

they may then be swept away and reentrained in the exit gas. The particles may even pick up positive charges from the collecting plate and then be repelled. Low-resistivity problems are common with dusts of high carbon content and may also occur in fly-ash precipitators which handle the ash from high-sulfur coal and operate at low gas temperatures. Low resistivity in this case results from excessive condensation of electrically conductive sulfuric acid.

Single-Stage Precipitators The single-stage type of unit, commonly known as a Cottrell precipitator, is most generally used for dust or mist collection from industrial-process gases. The corona discharge is maintained throughout the precipitator and, besides providing initial ionization, serves to prevent redispersion of precipitated dust and recharges neutralized or discharged particle ions. Cottrell precipitators may be divided into two main classes, the so-called plate type (Fig. 17-70), in which the collecting electrodes consist of parallel plates, screens, or rows of rods, chains, or wires; and the pipe type (Fig. 17-71), in which the collecting electrodes consist of a nest of parallel pipes which may be square, round, or of any other shape. The discharge or precipitating electrodes in each case are wires or rods, either round or edged, which are placed midway between the collecting electrodes or in the center of the pipes and may be either parallel or perpendicular to the gas flow in the case of plate precipitators. When the collecting electrodes are screens or rows of rods or wires, the gases are usually passed parallel to the plane of each but may also be passed through it. In pipe precipitators, the gas flow is generally vertical up through the pipe, although downflow is not unusual. The pipe-type precipitator is usually used for the removal of liquid particles and volatilized fumes [Beaver, op. cit.; and Cree, *Am. Gas J.,* **162,** 27 (March 1945)], and the plate type is used mainly on dusts. In the pipe type, the discharge electrodes are usually suspended from an insulated support and kept taut by a weight at the bottom. Cree (op.

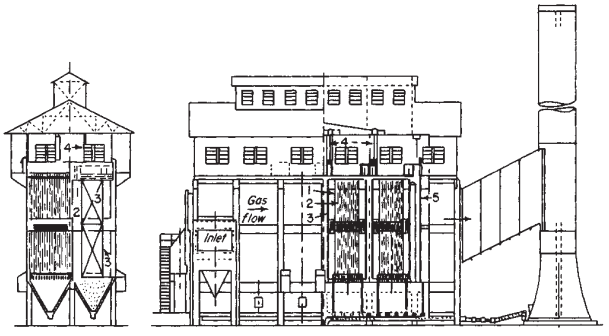


FIG. 17-70 Horizontal-flow plate precipitator used in a cement plant. (*Western Precipitation Division, Joy Manufacturing Company.*)

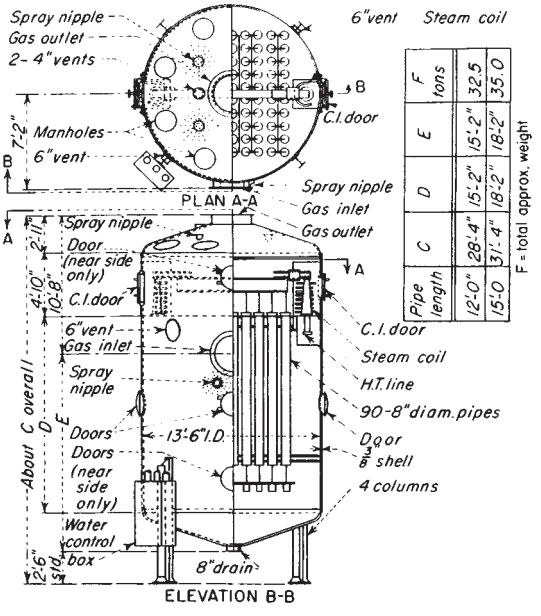


FIG. 17-71 Blast-furnace pipe precipitator. (*Research-Cottrell, Inc.*)

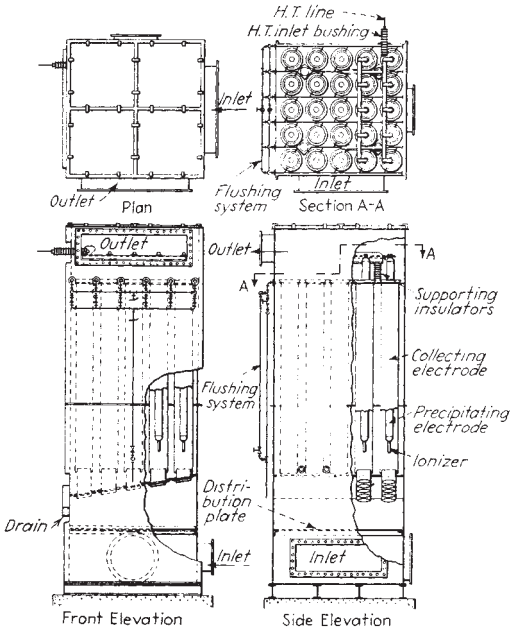


FIG. 17-72 Two-stage water-film pipe precipitator. (*Western Precipitation Division, Joy Manufacturing Company.*)

cit.) discusses the application of electrical precipitators to tar removal in the gas industry.

Rapping Except when liquid dispersoids are being collected or, in the case of film precipitators, when a liquid is circulated over the collecting-electrode surface (Fig. 17-72), thus continuously removing the precipitated material, the collected dust is dislodged from the electrodes either periodically or continuously by mechanical rapping or scraping, which may be performed automatically or manually. Automatic rapping with either impact-type or vibrator-type rappers is common practice. White (op. cit.) recommends fairly continuous rapping with magnetic-impulse rappers. Rapping with excessive force leads to dust reentrainment and possible mechanical failure of the plates, while insufficient rapping leads to excessive dust buildup with poor electrical operation and reduced collection efficiency. Intermittent rapping at intervals of an hour or more causes heavy puffs of reentrained dust. Sproull [*Air Pollut. Control Assoc. J.*, **15,** 50 (1965)] reports the importance of electrode acceleration and shows that it varies with the type of dust, whether the electrode is rapped perpendicularly (normally) to the plate or parallel to it. Figure 17-73 shows the accelerations required for rapping normally to the plate. Difficult dusts may require as much as 100 G acceleration for 90 percent removal, and even higher accelerations are required when the vibrating force is applied in the plane of the plate.

Perforated-plate or rod-curtain precipitators are frequently rapped without shutting off the gas flow and with the electrodes energized. This procedure, however, results in a tendency for reentrainment of collected dust. Sectional or composite-plate collecting electrodes (sometimes known as hollow, pocket, or tulip electrodes) are used to minimize this tendency in the continuous removal of the precipitated material, provided that it is free-flowing. These are generally designed for vertical gas flow and comprise a collecting electrode containing a dead air space and provided with horizontal protruding slots that guide the dust into this space (see Fig. 17-74), although some types use horizontal flow.

The choice of size, shape, and type of electrode is based on economic considerations and is usually determined by the characteristics of the gas and suspended matter and by mechanical considerations such as flue arrangement, the available space, and previous experience with the electrodes on similar problems. The spacing between collecting electrodes in plate-type precipitators and the pipe diameter

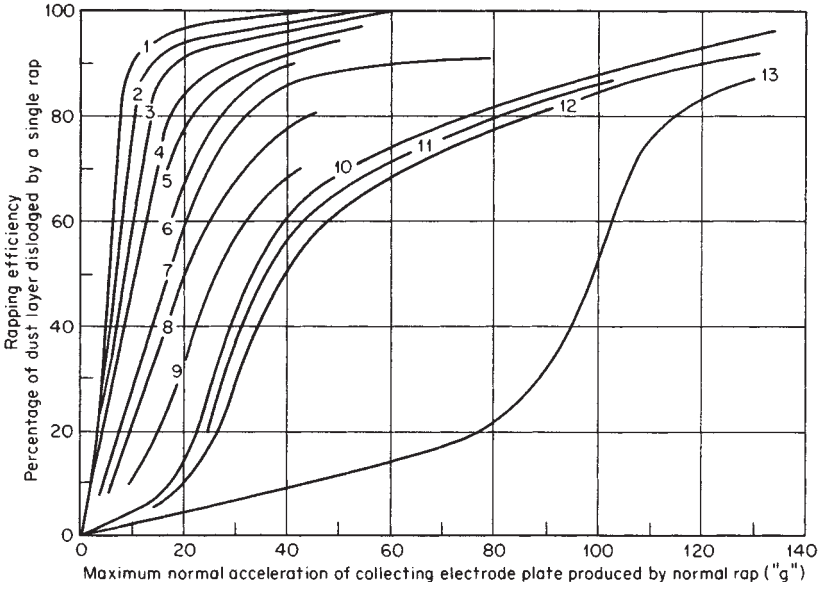


FIG. 17-73 Normal (perpendicular) rapping efficiency for various precipitated dust layers having about 0.03 g dust/cm^2 (0.2 g dust/in^2) as a function of maximum acceleration in multiples of *g*. Curve 1, fly ash, 200 or 300°F, power off. Curve 2, fly ash, 70°F, power off; also 200 or 300°F, power on. Curve 3, fly ash, 70°F, power on. Curve 4, cement-kiln feed, 300°F, power off. Curve 5, cement dust, 300°F, power off. Curve 6, same as 5, except power on. Curve 7, cement-kiln feed, 300°F, power on. Curve 8, cement dust, 200°F, power off. Curve 9, same as 8, except power on. Curve 10, cement-kiln feed, 200°F, power off. Curve 11, same as 10, except at 70°F. Curve 12, cement-kiln feed, 200°F, power on. Curve 13, cement-kiln feed, 70°F, power on. °C = (°F − 32) × 5/9. [*Sproull,* Air Pollut. Control Assoc. J., ***15,*** *50 (1965).*]

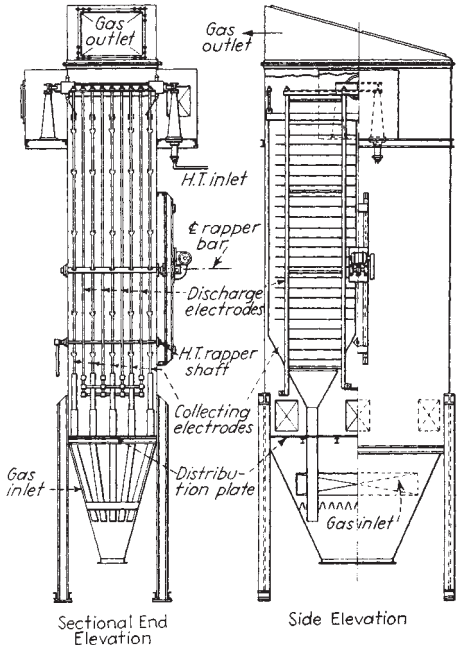


FIG. 17-74 Vertical-flow heavy-duty plate precipitator. (*Western Precipitation Division, Joy Manufacturing Company.*)

in pipe-type precipitators usually ranges from 15 to 38 cm (6 to 15 in). The smaller the spacing, the lower the necessary voltage and overall equipment size, but the greater the difficulties involved in maintaining proper alignment and resulting from disturbances due to collected material. Large spacings are usually associated with high dust concentration in order to minimize sparkover due to dust buildup. For very high dust concentrations, such as those encountered in fluid-catalyst plants, it is advantageous to use greater spacings in the first half of the precipitator than in the second half. Precipitators, especially of the plate type, are frequently built with groups of collecting electrodes in series in a common housing. Collecting electrodes are generally on the order of 0.9 to 1.8 m (3 to 6 ft) wide and 3 to 5.5 m (10 to 18 ft) high in plate-type precipitators and 1.8 to 4.6 m (6 to 15 ft) high in pipe types. It is essential for good collection efficiency that the gas be evenly distributed across the various electrode elements. Although this can be achieved by proper gas-inlet transitions and guide vanes, perforated plates or screens located on the upstream side of the electrodes are generally used for distribution. Perforated plates or screens located on the downstream side may be used in special cases.

Electrical precipitators are generally designed for collection efficiency in the range of 90 to 99.9 percent. It is essential, however, that the units be properly maintained in order to achieve the required collection efficiency. Electric power consumption is generally 0.2 to 0.6 kW/(1000 ft^3·min) of gas handled, and the pressure drop across the precipitator unit is usually less than 124 Pa (0.5 in water), ranging from 62 to 248 Pa (¼ to 1 in) and representing primarily distributor and entrance-exit losses. Applied potentials range from 30,000 to 100,000 V. Gas velocities and retention times are generally in the range of 0.9 to 3 m/s (3 to 10 ft/s) and 1 to 15 s respectively. Velocities are kept low in conventional precipitators to avoid reentrainment of dust. There are, however, precipitator installations on carbon black in which the precipitator acts to flocculate the dust so that it may be subsequently collected in multiple small-diameter cyclone collectors. By not attempting to collect the particles in the precipitator, higher velocities may be used with a correspondingly lower investment cost.

Power Supply Electrical precipitators are generally energized by rectified alternating current of commercial frequency. The voltage is stepped up to the required value by means of a transformer and then rectified. The rectifying equipment has undergone an evolution which began with the synchronous mechanical rectifier in 1904 and was followed by mercury-vapor rectifiers in the 1920s; the first solid-state selenium rectifiers were introduced about 1939. Silicon rectifiers are the latest and most widely used type, since they provide high efficiency and reliability. Automatic controls commonly are tied to voltage, current, spark rate, or some combination of these parameters. Modern precipitators use control circuits similar to those on Fig. 17-75. A high-voltage silicon rectifier is used together with a saturable reactor and means for limiting current and controlling voltage and/or spark rate. One popular method adjusts the voltage to give a specified sparking frequency (typically 50 to 150 sparks per minute per bus section). Half-wave rectification is sometimes used because of its lower equipment requirements and power consumption. It also has the advantage of longer decay periods for sparks to extinguish between current pulses.

Electrode **insulators** must also be designed for a particular service. The properties of the dust or mist and gas determine their design as well as the physical details of the installation. Conducting mists require special allowances such as oil seals, energized shielding cups, or air bleeds. With saturated gas, steam coils are frequently used to prevent condensation on the electrodes.

Typical applications in the chemical field (Beaver, op. cit.) include detarring of manufactured gas, removal of acid mist and impurities in contact sulfuric acid plants, recovery of phosphoric acid mists, removal of dusts in gases from roasters, sintering machines, calciners, cement and lime kilns, blast furnaces, carbon-black furnaces, regenerators on fluid-catalyst units, chemical-recovery furnaces in soda and sulfate pulp mills, and gypsum kettles. Figure 17-74 shows a vertical-flow steel-plate-type precipitator similar to a type used for catalyst-dust collection in certain fluid-catalyst plants.

A development of interest to the chemical industry is the tubular precipitator of reinforced-plastic construction (Wanner, *Gas Cleaning Plant after TiO_2 Rotary Kilns*, technical bulletin, Lurgi Corp., Frankfurt, Germany, 1971). Tubes made of polyvinyl chloride plastic are reinforced on the outside with polyester-fiber glass. The use of modern economical materials of construction to replace high-maintenance materials such as lead has been long awaited for corrosive applications.

Electrical precipitators are probably the most versatile of all types of dust collectors. Very high collection efficiencies can be obtained regardless of the fineness of the dust, provided that the precipitators are given proper maintenance. The chief disadvantages are the high initial cost and, in some cases, high maintenance costs. Furthermore, caution must be exercised with dusts that are combustible in the carrier gas.

Two-Stage Precipitators In two-stage precipitators, corona discharge takes place in the first stage between two electrodes having a nonuniform field (see Fig. 17-76). This is generally obtained by a fine-wire discharge electrode and a large-diameter receiving electrode. In this stage the potential difference must be above that required for corona discharge. The second stage involves a relatively uniform electrostatic field in which charged particles are caused to migrate to a collecting surface. This stage usually consists of either alternately charged parallel plates or concentric cylinders with relatively close clearances compared with their diameters. The only voltage requirement in this stage is that no sparking occur, though higher voltages will result in increased collection efficiency. Since collection occurs in the absence of corona discharge, there is no way of recharging reentrained and discharged particles. Consequently, some means must be provided for avoiding reentrainment of particles from the collecting surface. It is also essential that there be sufficient time and mixing between the first and second stages to secure distribution of gas ions across the gas stream and proper charging of the dust particles.

A unit is available in which electrostatic precipitation is combined with a dry-air filter of the type shown in Fig. 17-64*b*. In another unit an electrostatic field is superimposed on an automatic filter. In this case the ionizer wires are located on the leading face of the unit, and the collecting electrodes consist of alternate stationary and rotating parallel plates. Cleaning in this case is automatic and continuous.

Although intended primarily for air-conditioning applications, these units have been successfully applied to the collection of relatively nonconducting mists such as oil. However, other process applications

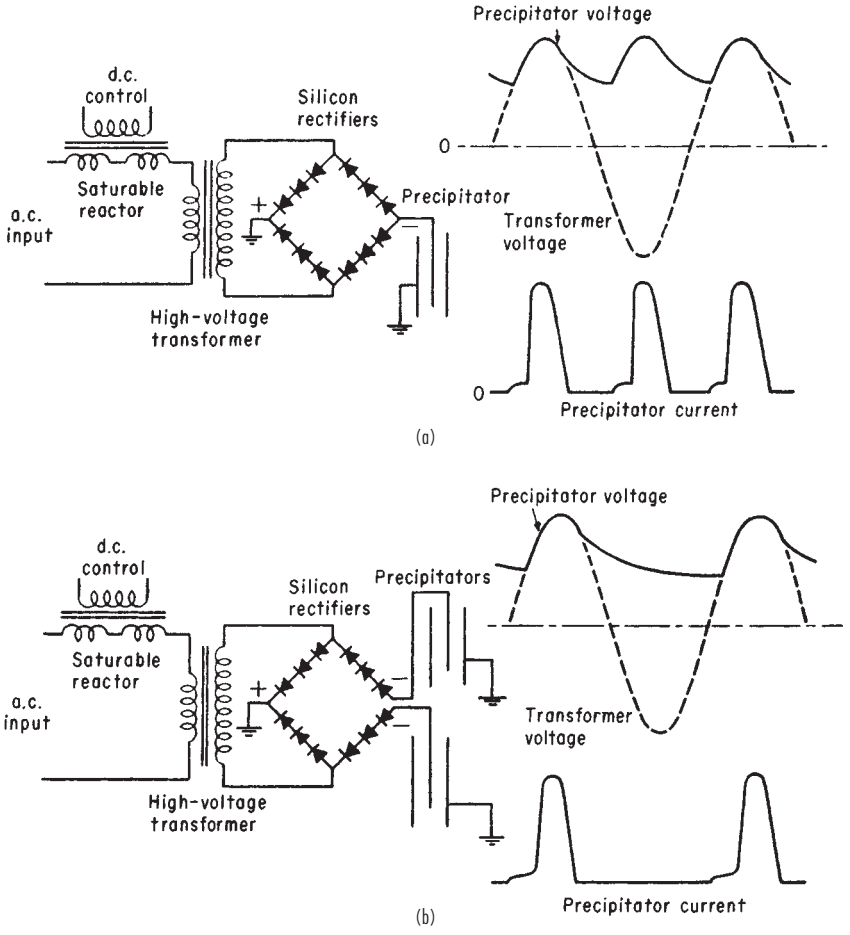


FIG. 17-75 Schematic circuits for silicon rectifier sets with saturable reactor control. (*a*) Full-wave silicon rectifier. (*b*) Half-wave silicon rectifier. (*White,* Industrial Electrostatic Precipitation, *Addison-Wesley, Reading, Mass., 1963.*)

have been limited largely to experimental installations. The large cost advantage of these units over the Cottrell precipitator lies in the smaller equipment size made possible by the close plate spacing, in the lower power consumption due to the two-stage operation, and primarily in the mass production of standardized units. In process applications, the close plate spacing is objectionable because of the relatively high dust concentrations involved. Special material or weight requirements for the structural members may eliminate the mass-production advantage except for individual wide applications.

Alternating-Current Precipitators High-voltage alternating current may be employed for electrical precipitation. Corona discharge will result in a net rectification, provided that no spark gaps are used in series with the precipitator. However, the equipment capacity for a given efficiency is considerably lower than for direct current. In addition, difficulties due to induced high-frequency currents may be encountered. The simplicity of an ac system, on the other hand, has permitted very satisfactory adaptation for laboratory and sampling purposes [Drinker, Thomson, and Fitchet, *J. Ind. Hyg.*, **5,** 162 (September 1923)].

Some promising work with alternating current has been undertaken at the University of Karlsruhe. Lau [*Staub,* English ed., **29,** 10 (1969)] and coworkers found that ac precipitators operated at 50 Hz were more effective than dc precipitators for dusts with resistivities higher than 10^{11} Ω·cm. An insulating screen covering the collecting electrode permitted higher-voltage operation without sparkover.

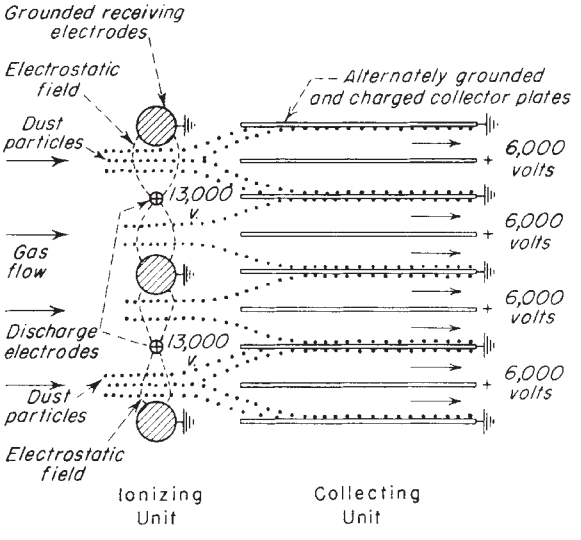


FIG. 17-76 Two-stage electrical-precipitation principle.

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Liquid-Solid Operations and Equipment

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Nomenclature

Symbol	Definition	SI units	U.S. customary units
c	Specific heat	J/(kg·k)	Btu/(lb·°F)
C	Constant		
C_o	Orifice coefficient	Dimensionless	Dimensionless
d_o	Orifice diameter	m	in
$d_{p,\,max}$	Drop diameter	m	ft
d_t	Pipe diameter	m	in
d_t	Tube diameter	m	ft
D	Impeller diameter	m	ft
D_a	Impeller diameter	m	ft
D_j	Diameter of jacketed vessel	m	ft
D_T	Tank diameter	m	ft
g	Acceleration	m/s^2	ft/s^2
g_c	Dimensional constant	$g_c = 1$ when using SI units	32.2 (ft·lb)/(lbf·s^2)
h	Local individual coefficient of heat transfer, equals $dq/(dA)(\Delta T)$	J/(m^2·s·K)	Btu/(h·ft^2·°F)
H	Velocity head	m	ft
k	Thermal conductivity	J/(m·s·K)	(Btu·ft)/(h·ft^2·°F)
L_p	Diameter of agitator blade	m	ft
N	Agitator rotational speed	s^{-1}, (r/s)	s^{-1}, (r/s)
N_{JS}	Agitator speed for just suspension	s^{-1}	s^{-1}
N_{Re}	$D_a^2 N\rho/\mu$ impeller Reynolds number	Dimensionless	Dimensionless
N_p	Power number = $(g_c P)/\rho N^3 D_a^5$	Dimensionless	Dimensionless
N_Q	Impeller pumping coefficient = Q/ND_a^3	Dimensionless	Dimensionless
N_r	Impeller speed	s^{-1}	s^{-1}
N_t	Impeller speed	s^{-1}	s^{-1}
P	Power	(N·m/s)	ft·lb$_f$/s
Q	Impeller flow rate	m^3/s	ft^3/s
T	Tank diameter	m	ft
v	Average fluid velocity	m/s	ft/s
v'	Fluid velocity fluctuation	m/s	ft/s
V	Bulk average velocity	m/s	ft/s
Z	Liquid level in tank	m	ft
	Greek symbols		
γ	Rate of shear	s^{-1}	s^{-1}
Δp	Pressure drop across orifice		lbf/ft^2
μ	Viscosity of liquid at tank temperature	Pa·s	lb/(ft·s)
μ	Stirred liquid viscosity	Pa·s	lb/(ft·s)
μ_b	Viscosity of fluid at bulk temperature	Pa·s	lb/(ft·s)
μ_c	Viscosity, continuous phase	Pa·s	lb/(ft·s)
μ_D	Viscosity of dispersed phase	Pa·s	lb/(ft·s)
μ_f	Viscosity of liquid at mean film temperature	Pa·s	lb/(ft·s)
μ_{wt}	Viscosity at wall temperature	Pa·s	lb/(ft·s)
ρ	Stirred liquid density	g/m^3	lb/ft^3
ρ	Density of fluid	kg/m^3	lb/ft^3
ρ_{av}	Density of dispersed phase	kg/m^3	lb/ft^3
ρ_c	Density	kg/m^3	lb/ft^3
σ	Interfacial tension	N/m	lbf/ft
Φ_D	Average volume fraction of discontinuous phase	Dimensionless	Dimensionless

PHASE CONTACTING AND LIQUID-SOLID PROCESSING: AGITATION OF LOW-VISCOSITY PARTICLE SUSPENSIONS

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FLUID MIXING TECHNOLOGY

Fluid mixers cut across almost every processing industry including the chemical process industry; minerals, pulp, and paper; waste and water treating and almost every individual process sector. The engineer working with the application and design of mixers for a given process has three basic sources for information. One is published literature, consisting of several thousand published articles and several currently available books, and brochures from equipment vendors. In addition, there may be a variety of in-house experience which may or may not be cataloged, categorized, or usefully available for the process application at hand. Also, short courses are currently available in selected locations and with various course objectives, and a large body of experience and information lies in the hands of equipment vendors.

In the United States, it is customary to design and purchase a mixer from a mixing vendor and purchase the vessel from another supplier. In many other countries, it is more common to purchase the vessel and mixer as a package from one supplier.

In any event, the users of the mixer can issue a mechanical specification and determine the speed, diameter of an impeller, and power with in-house expertise. Or they may issue a processes specification which describes the engineering purpose of the mixing operation and the vendor will supply a description of the mixer process performance as well as prepare a mechanical design.

This section describes fluid mixing technology and is referred to in other sections in this handbook which discuss the use of fluid mixing equipment in their various operating disciplines. This section does not describe paste and dough mixing, which may require planetary and extruder-type mixers, nor the area of dry solid-solid mixing.

It is convenient to divide mixing into five pairs (plus three triplets and one quadruplicate combination) of materials, as shown in Table 18-1. These five pairs are blending (miscible liquids), liquid-solid, liquid-gas, liquid-liquid (immiscible liquids), and fluid motion. There are also four other categories that occur, involving three or four phases. One concept that differentiates mixing requirements is the difference between physical criteria listed on the left side of Table 18-1, in which some degree of sampling can be used to determine the character of the mixture in various parts in the tank, and various definitions of mixing requirements can be based on these physical descriptions. The other category on the right side of Table 18-1 involves chemical and mass-transfer criteria in which rates of mass transfer or chemical reaction are of interest and have many more complexities in expressing the mixing requirements.

The first five classes have their own mixing technologies. Each of these 10 areas has its own mixing technology. There are relationships for the optimum geometry of impeller types, D/T ratios, and tank geometry. They each often have general, overall mixing requirements and different scale-up relationships based on process definitions. In addition, there are many subclassifications, some of which are based on the viscosity of fluids. In the case of blending, we have blending in the viscous region, the transition region, and the turbulent region. Since any given mixer designed for a process may be required to do several different parts of these 10 categories, it must be a compromise of the geometry and other requirements for the total process result and may not optimize any one particular process component. If it turns out that one particular process requirement is so predominant that all the other requirements are satisfied as a consequence, then it is possible to optimize that particular process step. Often, the only process requirement is in one of these 10 areas, and the mixer can be designed and optimized for that one step only.

As an example of the complexity of fluid mixing, many batch processes involve adding many different materials and varying the liquid level over wide ranges in the tank, have different temperatures and shear rate requirements, and obviously need experience and expert attention to all of the requirements. Superimpose the requirements for sound mechanical design, including drives, fluid seals, and rotating shafts, means that the concepts presented here are merely a beginning to the overall, final design.

A few general principles are helpful at this point before proceeding to the examination of equipment and process details. For any given impeller geometry, speed, and diameter, the impeller draws a certain amount of power. This power is 100 percent converted to heat. In low-viscosity mixing (defined later), this power is used to generate a *macro-scale* regime in which one typically has the visual observation of flow pattern, swirls, and other surface phenomena. However, these flow patterns are primarily energy transfer agents that transfer the power down to the micro scale. The macro-scale regime involves the pumping capacity of the impeller as well as the total circulating capacity throughout the tank and it is an important part of the overall mixer design. The micro-scale area in which the power is dissipated does not care much which impeller is used to generate the energy dissipation. In contrast, in high-viscosity processes, there is a continual progress of energy dissipation from the macro scale down to the micro scale.

There is a wide variety of impellers using *fluidfoil principles,* which are used when flow from the impeller is predominant in the process requirement and macro- or micro-scale shear rates are a subordinate issue.

Scale-up involves selecting mixing variables to give the desired performance in both pilot and full scale. This is often difficult (sometimes

TABLE 18-1 Classification System for Mixing Processes

Physical	Components	Chemical, mass transfer
Blending	Blending	Chemical reactions
Suspension	Solid-liquid	Dissolving, precipitation
Dispersion	Gas-liquid	Gas absorption
	Solid-liquid-gas	
Emulsions	Liquid-liquid	Extraction
	Liquid-liquid-solid	
	Gas-liquid-liquid	
	Gas-liquid-liquid-solid	
Pumping	Fluid motion	Heat transfer

impossible) using geometric similarity, so that the use of nongeometric impellers in the pilot plant compared to the impellers used in the plant often allows closer modeling of the mixing requirements to be achieved.

Computational fluid mixing allows the modeling of flow patterns in mixing vessels and some of the principles on which this is based in current techniques are included.

INTRODUCTORY FLUID MECHANICS

The fluid mixing process involves three different areas of viscosity which affect flow patterns and scale-up, and two different scales within the fluid itself: macro scale and micro scale. Design questions come up when looking at the design and performance of mixing processes in a given volume. Considerations must be given to proper impeller and tank geometry as well as the proper speed and power for the impeller. Similar considerations come up when it is desired to scale up or scale down, and this involves another set of mixing considerations.

If the fluid discharge from an impeller is measured with a device that has a high-frequency response, one can track the velocity of the fluid as a function of time. The velocity at a given point in time can then be expressed as an average velocity v plus fluctuating component v'. Average velocities can be integrated across the discharge of the impeller, and the pumping capacity normal to an arbitrary discharge plane can be calculated. This arbitrary discharge plane is often defined as the plane bounded by the boundaries of the impeller blade diameter and height. Because there is no casing, however, an additional 10 to 20 percent of flow typically can be considered as the primary flow from an impeller.

The velocity gradients between the average velocities operate only on larger particles. Typically, these larger-size particles are greater than 1000 μm. This is not a proven definition, but it does give a feel for the magnitudes involved. This defines macro-scale mixing. In the turbulent region, these macro-scale fluctuations can also arise from the finite number of impeller blades. These set up velocity fluctuations that can also operate on the macro scale.

Smaller particles see primarily only the fluctuating velocity component. When the particle size is much less than 100 μm, the turbulent properties of the fluid become important. This is the definition of the physical size for micro-scale mixing.

All of the power applied by a mixer to a fluid through the impeller appears as heat. The conversion of power to heat is through viscous shear and is approximately 2542 Btu/h/hp. Viscous shear is present in turbulent flow only at the micro-scale level. As a result, the power per unit volume is a major component of the phenomena of micro-scale mixing. At a 1-μm level, in fact, it doesn't matter what specific impeller design is used to supply the power.

Numerous experiments show that power per unit volume in the zone of the impeller (which is about 5 percent of the total tank volume) is about 100 times higher than the power per unit volume in the rest of the vessel. Making some reasonable assumptions about the fluid mechanics parameters, the root-mean-square (rms) velocity fluctuation in the zone of the impeller appears to be approximately 5 to 10 times higher than in the rest of the vessel. This conclusion has been verified by experimental measurements.

The ratio of the rms velocity fluctuation to the average velocity in the impeller zone is about 50 percent with many open impellers. If the rms velocity fluctuation is divided by the average velocity in the rest of the vessel, however, the ratio is on the order of 5 percent. This is also the level of rms velocity fluctuation to the mean velocity in pipeline flow. There are phenomena in micro-scale mixing that can occur in mixing tanks that do not occur in pipeline reactors. Whether this is good or bad depends upon the process requirements.

Figure 18-1 shows velocity versus time for three different impellers. The differences between the impellers are quite significant and can be important for mixing processes.

All three impellers are calculated for the same impeller flow Q and the same diameter. The A310 (Fig. 18-2) draws the least power and has the least velocity fluctuations. This gives the lowest micro-scale turbulence and shear rate. The A200 (Fig. 18-3) shows increased velocity

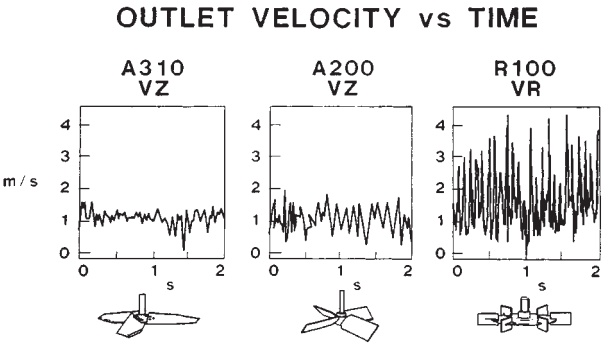


FIG. 18-1 Velocity fluctuations versus time for equal total pumping capacity from three different impellers.

fluctuations and draws more power. The R100 (Fig. 18-4) draws the most power and has the highest micro-scale shear rate. The proper impeller should be used for each individual process requirement.

Scale-up/Scale-down Two aspects of scale-up frequently arise. One is building a model based on pilot-plant studies that develop an understanding of the process variables for an existing full-scale mixing installation. The other is taking a new process and studying it in the pilot plant in such a way that pertinent scale-up variables are worked out for a new mixing installation.

There are a few principles of scale-up that can indicate which approach to take in either case. Using geometric similarity, the macro-scale variables can be summarized as follows:

- Blend and circulation times in the large tank will be much longer than in the small tank.



FIG. 18-2 An A310 impeller.

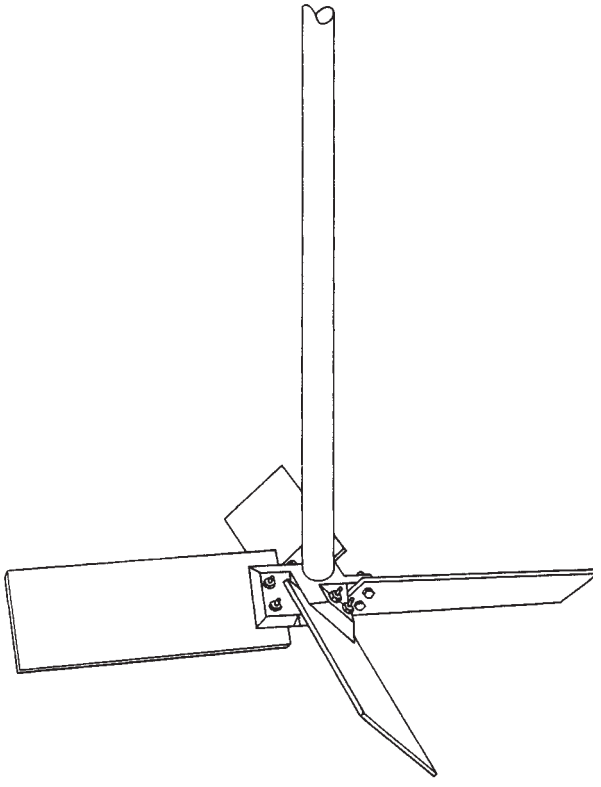


FIG. 18-3 Pitched-blade turbine.

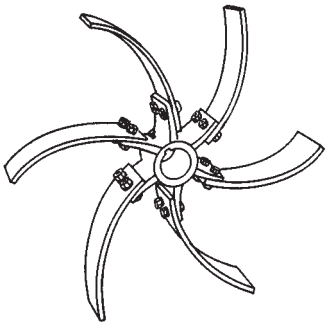


FIG. 18-4 Flat-blade turbine.

• Maximum impeller zone shear rate will be higher in the larger tank, but the average impeller zone shear rate will be lower; therefore, there will be a much greater variation in shear rates in a full-scale tank than in a pilot unit.

• Reynolds numbers in the large tank will be higher, typically on the order of 5 to 25 times higher than those in a small tank.

• Large tanks tend to develop a recirculation pattern from the impeller through the tank back to the impeller. This results in a behavior similar to that for a number of tanks in a series. The net result is that the mean circulation time is increased over what would be predicted from the impeller pumping capacity. This also increases the standard deviation of the circulation times around the mean.

• Heat transfer is normally much more demanding on a large scale. The introduction of helical coils, vertical tubes, or other heat-transfer devices causes an increased tendency for areas of low recirculation to exist.

• In gas-liquid systems, the tendency for an increase in the gas superficial velocity upon scale-up can further increase the overall circulation time.

What about the micro-scale phenomena? These are dependent primarily on the energy dissipation per unit volume, although one must also be concerned about the energy spectra. In general, the energy dissipation per unit volume around the impeller is approximately 100 times higher than in the rest of the tank. This results in an rms velocity fluctuation ratio to the average velocity on the order of 10:1 between the impeller zone and the rest of the tank.

Because there are thousands of specific processes each year that involve mixing, there will be at least hundreds of different situations requiring a somewhat different pilot-plant approach. Unfortunately, no set of rules states how to carry out studies for any specific program, but here are a few guidelines that can help one carry out a pilot-plant program.

• For any given process, one takes a qualitative look at the possible role of fluid shear stresses. Then one tries to consider pathways related to fluid shear stress that may affect the process. If there are none, then this extremely complex phenomenon can be dismissed and the process design can be based on such things as uniformity, circulation time, blend time, or velocity specifications. This is often the case in the blending of miscible fluids and the suspension of solids.

• If fluid shear stresses are likely to be involved in obtaining a process result, then one must qualitatively look at the scale at which the shear stresses influence the result. If the particles, bubbles, droplets, or fluid clumps are on the order of 1000 μm or larger, the variables are macro scale and average velocities at a point are the predominant variable.

When macro-scale variables are involved, every geometric design variable can affect the role of shear stresses. They can include such items as power, impeller speed, impeller diameter, impeller blade shape, impeller blade width or height, thickness of the material used to make the impeller, number of blades, impeller location, baffle location, and number of impellers.

Micro-scale variables are involved when the particles, droplets, baffles, or fluid clumps are on the order of 100 μm or less. In this case, the critical parameters usually are power per unit volume, distribution of power per unit volume between the impeller and the rest of the tank, rms velocity fluctuation, energy spectra, dissipation length, the smallest micro-scale eddy size for the particular power level, and viscosity of the fluid.

• The overall circulating pattern, including the circulation time and the deviation of the circulation times, can never be neglected. No matter what else a mixer does, it must be able to circulate fluid throughout an entire vessel appropriately. If it cannot, then that mixer is not suited for the task being considered.

Qualitative and, hopefully, quantitative estimates of how the process result will be measured must be made in advance. The evaluations must allow one to establish the importance of the different steps in a process, such as gas-liquid mass transfer, chemical reaction rate, or heat transfer.

• It is seldom possible, either economically or timewise, to study every potential mixing variable or to compare the performance of many impeller types. In many cases, a process needs a specific fluid regime that is relatively independent of the impeller type used to generate it. Because different impellers may require different geometries to achieve an optimum process combination, a random choice of only one diameter of each of two or more impeller types may not tell what is appropriate for the fluid regime ultimately required.

• Often, a pilot plant will operate in the viscous region while the commercial unit will operate in the transition region, or alternatively, the pilot plant may be in the transition region and the commercial unit in the turbulent region. Some experience is required to estimate the difference in performance to be expected upon scale-up.

• In general, it is not necessary to model Z/T ratios between pilot and commercial units.

• In order to make the pilot unit more like a commercial unit in macro-scale characteristics, the pilot unit impeller must be designed

to lengthen the blend time and to increase the maximum impeller zone shear rate. This will result in a greater range of shear rates than is normally found in a pilot unit.

MIXING EQUIPMENT

There are three types of mixing flow patterns that are markedly different. The so-called axial-flow turbines (Fig. 18-3) actually give a flow coming off the impeller of approximately 45°, and therefore have a recirculation pattern coming back into the impeller at the hub region of the blades. This flow pattern exists to an approximate Reynolds number of 200 to 600 and then becomes radial as the Reynolds number decreases. Both the R100 and A200 impellers normally require four baffles for an effective flow pattern. These baffles typically are 1/12 of the tank diameter and width.

Radial-flow impellers include the flat-blade disc turbine, Fig. 18-4, which is labeled an R100. This generates a radial flow pattern at all Reynolds numbers. Figure 18-17 is the diagram of Reynolds number/power number curve, which allows one to calculate the power knowing the speed and diameter of the impeller. The impeller shown in Fig. 18-4 typically gives high shear rates and relatively low pumping capacity.

The current design of fluidfoil impellers includes the A310 (Fig. 18-2), as well as several other impellers of that type commonly referred to as *high-efficiency impellers*, *hydrofoil*, and other descriptive names to illustrate that they are designed to maximize flow and minimize shear rate. These impellers typically require two baffles, but are normally used with three, since three gives a more stable flow pattern. Since most industrial mixing processes involve pumping capacity and, to a lesser degree, fluid shear rate, the fluidfoil impellers are now used on the majority of the mixer installations. There is now an additional family of these fluidfoil impellers, which depend upon different solidity ratios to operate in various kinds of fluid mixing systems. Figure 18-5 illustrates four of these impellers. The solidity ratio is the ratio of total blade area to a circle circumscribing the impeller and, as viscosity increases, higher values of the solidity ratios are more effective in providing an axial flow pattern rather than a radial flow pattern. Also the A315-type provides an effective area of preventing gas bypassing through the hub of the impeller by having exceptionally wide blades. Another impeller of that type is the Prochem Maxflo T.

Small Tanks For tanks less than 1.8 m in diameter, the clamp or flanged mounted angular, off-center axial-flow impeller without baffles should be used for a wide range of process requirements (refer to Fig. 18-14). The impellers currently used are the fluidfoil type. Since small impellers typically operate at low Reynolds numbers, often in the transition region, the fluidfoil impeller should be designed to give good flow characteristics over a range of Reynolds numbers, probably on the order of 50 to 500. The Z/T ratio should be 0.75 to 1.5. The volume of liquid should not exceed 4 m^3.

Close-Clearance Impellers There are two close-clearance impellers. They are the *anchor impeller* (Fig. 18-6) and the *helical impeller* (Fig. 18-7), which operate near the tank wall and are particularly effective in pseudoplastic fluids in which it is desirable to have the mixing energy concentrated out near the tank wall where the flow pattern is more effective than with the open impellers that were covered earlier.

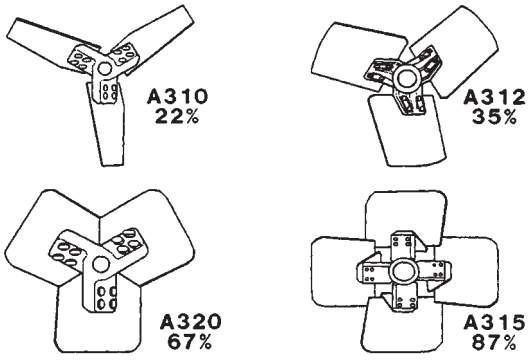


FIG. 18-5 The solidity ratio for four different impellers of the axial-flow fluidfoil type.

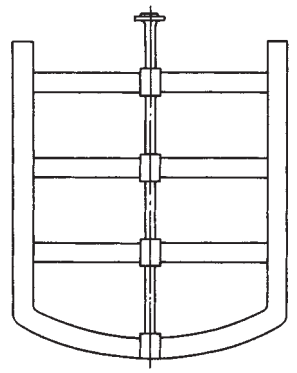


FIG. 18-6 Anchor impeller.

Axial-Flow Impellers Axial-flow impellers include all impellers in which the blade makes an angle of less than 90° with the plane of rotation. Propellers and pitched-blade turbines, as illustrated in Figs. 18-8 and 18-3, are representative axial-flow impellers.

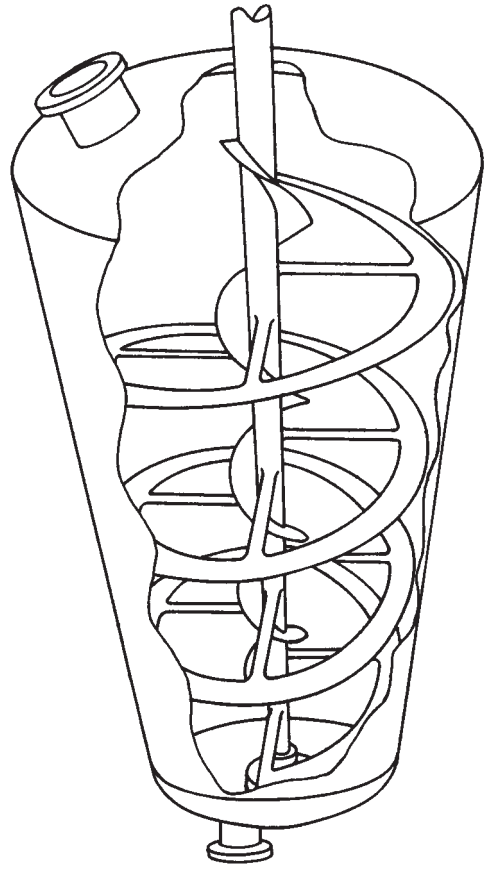


FIG. 18-7 Helical mixer for high-viscosity fluid.

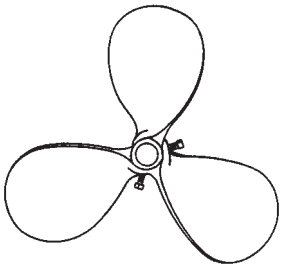


FIG. 18-8 Marine-type mixing impeller.

Portable mixers may be clamped on the side of an open vessel in the angular, off-center position shown in Fig. 18-14 or bolted to a flange or plate on the top of a closed vessel with the shaft in the same angular, off-center position. This mounting results in a strong top-to-bottom circulation.

Two basic speed ranges are available: 1150 or 1750 r/min with direct drive and 350 or 420 r/min with a gear drive. The high-speed units produce higher velocities and shear rates (Fig. 18-9) in the impeller discharge stream and a lower circulation rate throughout the vessel than the low-speed units. For suspension of solids, it is common to use the gear-driven units, while for rapid dispersion or fast reactions the high-speed units are more appropriate.

Axial-flow impellers may also be mounted near the bottom of the cylindrical wall of a vessel as shown in Fig. 18-10. Such side-entering agitators are used to blend low-viscosity fluids [<0.1 Pa·s (100 cP)] or to keep slowly settling sediment suspended in tanks as large as some 4000 m^3 (10^6 gal). Mixing of paper pulp is often carried out by side-entering propellers.

Pitched-blade turbines (Fig. 18-3) are used on top-entering agitator shafts instead of propellers when a high axial circulation rate is desired and the power consumption is more than 2.2 kW (3 hp). A pitched-blade turbine near the upper surface of liquid in a vessel is effective for rapid submergence of floating particulate solids.

Radial-Flow Impellers Radial-flow impellers have blades which are parallel to the axis of the drive shaft. The smaller multiblade ones are known as *turbines*; larger, slower-speed impellers, with two or four blades, are often called *paddles*. The diameter of a turbine is normally between 0.3 and 0.6 of the tank diameter. Turbine impellers come in a variety of types, such as curved-blade and flat-blade, as illustrated in Fig. 18-4. Curved blades aid in starting an impeller in settled solids.

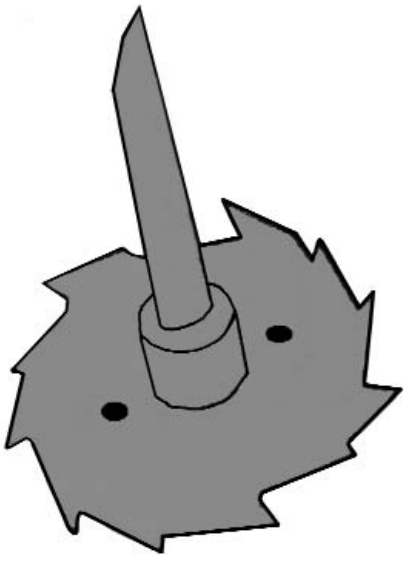


FIG. 18-9 High shear rate impeller.

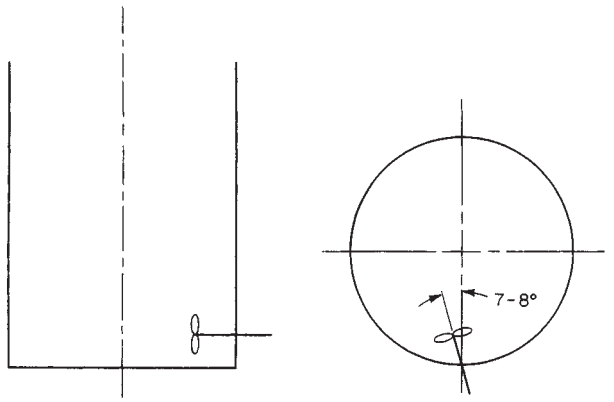


FIG. 18-10 Side-entering propeller mixer.

For processes in which corrosion of commonly used metals is a problem, glass-coated impellers may be economical. A typical modified curved-blade turbine of this type is shown in Fig. 18-11.

Close-Clearance Stirrers For some pseudoplastic fluid systems stagnant fluid may be found next to the vessel walls in parts remote from propeller or turbine impellers. In such cases, an "anchor" impeller may be used (Fig. 18-6). The fluid flow is principally circular or helical (see Fig. 18-7) in the direction of rotation of the anchor. Whether substantial axial or radial fluid motion also occurs depends on the fluid viscosity and the design of the upper blade-supporting spokes. Anchor agitators are used particularly to obtain improved heat transfer in high-consistency fluids.

Unbaffled Tanks If a low-viscosity liquid is stirred in an unbaffled tank by an axially mounted agitator, there is a tendency for a swirling flow pattern to develop regardless of the type of impeller. Figure 18-12 shows a typical flow pattern. A vortex is produced owing to centrifugal force acting on the rotating liquid. In spite of the presence of a vortex, satisfactory process results often can be obtained in an unbaffled vessel. However, there is a limit to the rotational speed that may be used, since once the vortex reaches the impeller, severe air entrainment may occur. In addition, the swirling mass of liquid often generates an oscillating surge in the tank, which coupled with the deep vortex may create a large fluctuating force acting on the mixer shaft.

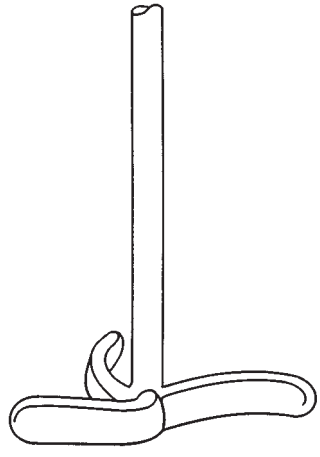


FIG. 18-11 Glass-steel impeller. (*The Pfaudler Company.*)

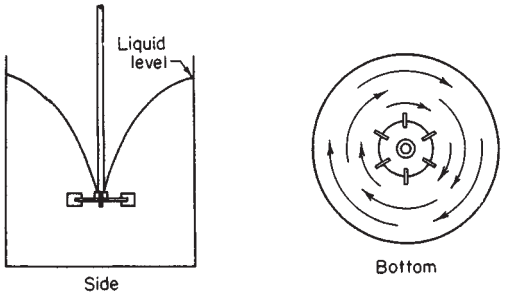


FIG. 18-12 Typical flow pattern for either axial- or radial-flow impellers in an unbaffled tank.

Vertical velocities in a vortexing low-viscosity liquid are low relative to circumferential velocities in the vessel. Increased vertical circulation rates may be obtained by mounting the impeller off center, as illustrated in Fig. 18-13. This position may be used with either turbines or propellers. The position is critical, since too far or too little off center in one direction or the other will cause greater swirling, erratic vortexing, and dangerously high shaft stresses. Changes in viscosity and tank size also affect the flow pattern in such vessels. Off-center mountings have been particularly effective in the suspension of paper pulp.

With axial-flow impellers, an angular off-center position may be used. The impeller is mounted approximately 15° from the vertical, as shown in Fig. 18-14.

The angular off-center position used with fluidfoil units is usually limited to impellers delivering 2.2 kW (3 hp) or less. The unbalanced fluid forces generated by this mounting can become severe with higher power.

Baffled Tanks For vigorous agitation of thin suspensions, the tank is provided with baffles which are flat vertical strips set radially along the tank wall, as illustrated in Figs. 18-15 and 18-16. Four baffles are almost always adequate. A common baffle width is one-tenth to one-twelfth of the tank diameter (radial dimension). For agitating slurries, the baffles often are located one-half of their width from the vessel wall to minimize accumulation of solids on or behind them.

For Reynolds numbers greater than 2000 baffles are commonly used with turbine impellers and with on-centerline axial-flow impellers. The flow patterns illustrated in Figs. 18-15 and 18-16 are quite different, but in both cases the use of baffles results in a large top-to-bottom circulation without vortexing or severely unbalanced fluid forces on the impeller shaft.

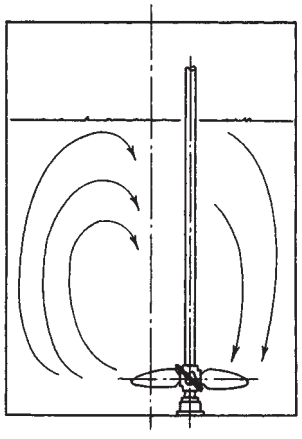


FIG. 18-13 Flow pattern with a paper-stock propeller, unbaffled; vertical off-center position.

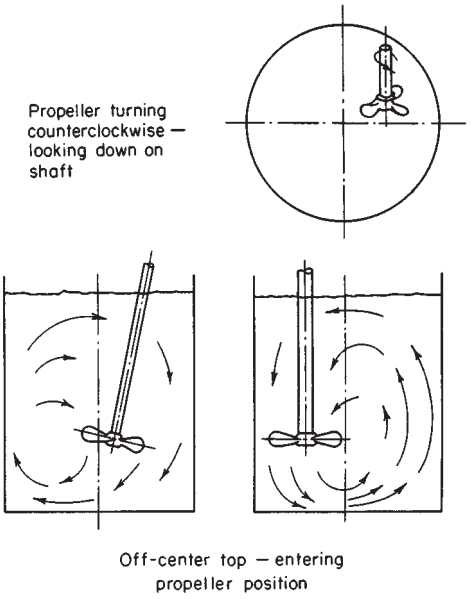


FIG. 18-14 Typical flow pattern with a propeller in angular off-center position without baffles.

In the transition region [Reynolds numbers, Eq. (18-1), from 10 to 10,000], the width of the baffle may be reduced, often to one-half of standard width. If the circulation pattern is satisfactory when the tank is unbaffled but a vortex creates a problem, partial-length baffles may be used. These are standard-width and extend downward from the surface into about one-third of the liquid volume.

In the region of laminar flow ($N_{Re} < 10$), the same power is consumed by the impeller whether baffles are present or not, and they are seldom required. The flow pattern may be affected by the baffles, but not always advantageously. When they are needed, the baffles are usually placed one or two widths radially off the tank wall, to allow fluid to circulate behind them and at the same time produce some axial deflection of flow.

FLUID BEHAVIOR IN MIXING VESSELS

Impeller Reynolds Number The presence or absence of turbulence in an impeller-stirred vessel can be correlated with an impeller Reynolds number defined

$$N_{Re} = \frac{D_a^2 N \rho}{\mu} \qquad (18\text{-}1)$$

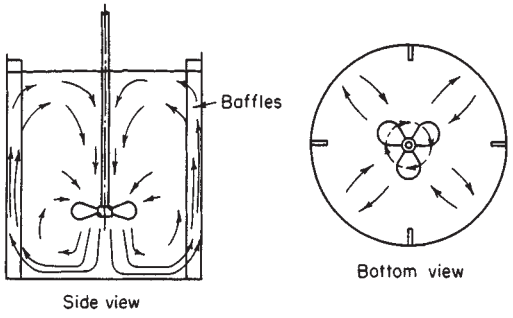


FIG. 18-15 Typical flow pattern in a baffled tank with a propeller or an axial-flow turbine positioned on center.

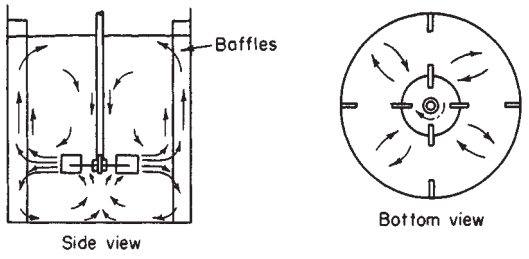


FIG. 18-16 Typical flow pattern in a baffled tank with a turbine positioned on center.

where N = rotational speed, r/s; D_a = impeller diameter, m (ft); ρ = fluid density, kg/m^3 (lb/ft^3); and μ = viscosity, Pa·s [lb/(ft·s)]. Flow in the tank is turbulent when $N_{Re} > 10{,}000$. Thus viscosity alone is not a valid indication of the type of flow to be expected. Between Reynolds numbers of 10,000 and approximately 10 is a transition range in which flow is turbulent at the impeller and laminar in remote parts of the vessel; when $N_{Re} < 10$, flow is laminar only.

Not only is the type of flow related to the impeller Reynolds number, but also such process performance characteristics as mixing time, impeller pumping rate, impeller power consumption, and heat- and mass-transfer coefficients can be correlated with this dimensionless group.

Relationship between Fluid Motion and Process Performance Several phenomena which can be used to promote various processing objectives occur during fluid motion in a vessel.

1. Shear stresses are developed in a fluid when a layer of fluid moves faster or slower than a nearby layer of fluid or a solid surface. In laminar flow, the shear stress is equal to the product of fluid viscosity and velocity gradient or rate of shear. Under laminar-flow conditions, shear forces are larger than inertial forces in the fluid.

With turbulent flow, shear stress also results from the behavior of transient random eddies, including large-scale eddies which decay to small eddies or fluctuations. The scale of the large eddies depends on equipment size. On the other hand, the scale of small eddies, which dissipate energy primarily through viscous shear, is almost independent of agitator and tank size.

The shear stress in the fluid is much higher near the impeller than it is near the tank wall. The difference is greater in large tanks than in small ones.

2. Inertial forces are developed when the velocity of a fluid changes direction or magnitude. In turbulent flow, inertia forces are larger than viscous forces. Fluid in motion tends to continue in motion until it meets a solid surface or other fluid moving in a different direction. Forces are developed during the momentum transfer that takes place. The forces acting on the impeller blades fluctuate in a random manner related to the scale and intensity of turbulence at the impeller.

3. The interfacial area between gases and liquids, immiscible liquids, and solids and liquids may be enlarged or reduced by these viscous and inertia forces when interacting with interfacial forces such as surface tension.

4. Concentration and temperature differences are reduced by bulk flow or circulation in a vessel. Fluid regions of different composition or temperature are reduced in thickness by bulk motion in which velocity gradients exist. This process is called bulk diffusion or Taylor diffusion (Brodkey, in Uhl and Gray, op. cit., vol. 1, p. 48). The turbulent and molecular diffusion reduces the difference between these regions. In laminar flow, Taylor diffusion and molecular diffusion are the mechanisms of concentration- and temperature-difference reduction.

5. Equilibrium concentrations which tend to develop at solid-liquid, gas-liquid, or liquid-liquid interfaces are displaced or changed by molecular and turbulent diffusion between bulk fluid and fluid adjacent to the interface. Bulk motion (Taylor diffusion) aids in this mass-transfer mechanism also.

Turbulent Flow in Stirred Vessels Turbulence parameters such as intensity and scale of turbulence, correlation coefficients, and energy spectra have been measured in stirred vessels. However, these characteristics are not used directly in the design of stirred vessels.

Fluid Velocities in Mixing Equipment Fluid velocities have been measured for various turbines in baffled and unbaffled vessels. Typical data are summarized in Uhl and Gray, op. cit., vol. 1, chap. 4. Velocity data have been used for calculating impeller discharge and circulation rates but are not employed directly in the design of mixing equipment.

Impeller Discharge Rate and Fluid Head for Turbulent Flow When fluid viscosity is low and flow is turbulent, an impeller moves fluids by an increase in momentum from the blades which exert a force on the fluid. The blades of rotating propellers and turbines change the direction and increase the velocity of the fluids.

The pumping rate or discharge rate of an impeller is the flow rate perpendicular to the impeller discharge area. The fluid passing through this area has velocities proportional to the impeller peripheral velocity and velocity heads proportional to the square of these velocities at each point in the impeller discharge stream under turbulent-flow conditions. The following equations relate velocity head, pumping rate, and power for geometrically similar impellers under turbulent-flow conditions:

$$Q = N_Q N D_a^3 \tag{18-2}$$

$$H = \frac{N_p N^2 D_a^2}{N_Q g} \tag{18-3}$$

$$P = N_p \rho N^3 \left(\frac{D_a^5}{g_c} \right) \tag{18-4}$$

$$P = \frac{\rho H Q g}{g_c} \tag{18-5}$$

where Q = impeller discharge rate, m^3/s (ft^3/s); N_Q = discharge coefficient, dimensionless; H = velocity head, m (ft); N_p = power number, dimensionless; P = power, (N·m)/s [(ft·lbf)/s]; g_c = dimensional constant, 32.2 (ft·lb)/(lbf·s^2)(g_c = 1 when using SI units); and g = gravitational acceleration, m/s^2 (ft/s^2).

The discharge rate Q has been measured for several types of impellers, and discharge coefficients have been calculated. The data of a number of investigators are reviewed by Uhl and Gray (op. cit., vol. 1, chap. 4). N_Q is 0.4 to 0.5 for a propeller with pitch equal to diameter at $N_{Re} = 10^5$. For turbines, N_Q ranges from 0.7 to 2.9, depending on the number of blades, blade-height-to-impeller-diameter ratio, and impeller-to-vessel-diameter ratio. The effects of these geometric variables are not well defined.

Power consumption has also been measured and correlated with impeller Reynolds number. The velocity head for a mixing impeller can be calculated, then, from flow and power data, by Eq. (18-3) or Eq. (18-5).

The velocity head of the impeller discharge stream is a measure of the maximum force that this fluid can exert when its velocity is changed. Such inertia forces are higher in streams with higher discharge velocities. Shear rates and shear stresses are also higher under these conditions in the smallest eddies. If a higher discharge velocity is desired at the same power consumption, a smaller-diameter impeller must be used at a higher rotational speed. According to Eq. (18-4), at a given power level $N \propto D_a^{-5/3}$ and $ND_a \propto D_a^{-2/3}$. Then, $H \propto D_a^{-4/3}$ and $Q \propto D_a^{4/3}$.

An impeller with a high fluid head is one with high peripheral velocity and discharge velocity. Such impellers are useful for (1) rapid reduction of concentration differences in the impeller discharge stream (rapid mixing), (2) production of large interfacial area and small droplets in gas-liquid and immiscible-liquid systems, (3) solids deagglomeration, and (4) promotion of mass transfer between phases.

The impeller discharge rate can be increased at the same power consumption by increasing impeller diameter and decreasing rotational speed and peripheral velocity so that $N^3 D_a^5$ is a constant (Eq. 18-4)]. Flow goes up, velocity head and peripheral velocity go down, but impeller torque T_Q goes up. At the same torque, $N^2 D_a^5$ is constant, $P \propto D_a^{-5/2}$, and $Q \propto D_a^{1/2}$. Therefore, increasing impeller diameter at constant torque increases discharge rate at lower power consumption. At the same discharge rate, ND_a^3 is constant, $P \propto D_a^{-4}$, and $T_Q \propto D_a^{-1}$.

Therefore, power and torque decrease as impeller diameter is increased at constant Q.

A large-diameter impeller with a high discharge rate is used for (1) short times to complete mixing of miscible liquid throughout a vessel, (2) promotion of heat transfer, (3) reduction of concentration and temperature differences in all parts of vessels used for constant-environment reactors and continuous averaging, and (4) suspension of particles of relatively low settling rate.

Laminar Fluid Motion in Vessels When the impeller Reynolds number is less than 10, the flow induced by the impeller is laminar. Under these conditions, the impeller drags fluid with it in a predominantly circular pattern. If the impeller blades curve back, there is a viscous drag flow toward the tips of these blades. Under moderate-viscosity conditions in laminar flow, centrifugal force acting on the fluid layer dragged in a circular path by the rotating impeller will move fluid in a radial direction. This centrifugal effect causes any gas accumulated behind a rotating blade to move to the axis of impeller rotation. Such radial-velocity components are small relative to tangential velocity.

For turbines at Reynolds numbers less than 100, toroidal stagnant zones exist above and below the turbine periphery. Interchange of liquid between these regions and the rest of the vessel is principally by molecular diffusion.

Suspensions of fine solids may have pseudoplastic or plastic-flow properties. When they are in laminar flow in a stirred vessel, motion in remote parts of the vessel where shear rates are low may become negligible or cease completely. To compensate for this behavior of slurries, large-diameter impellers or paddles are used, with $(D_a/D_T) > 0.6$, where D_T is the tank diameter. In some cases, for example, with some anchors, $D_a > 0.95\ D_T$. Two or more paddles may be used in deep tanks to avoid stagnant regions in slurries.

In laminar flow ($N_{Re} < 10$), $N_p \propto 1/N_{Re}$ and $P \propto \mu N^2 D_a^3$. Since shear stress is proportional to rotational speed, shear stress can be increased at the same power consumption by increasing N proportionally to $D_a^{-3/2}$ as impeller diameter D_a is decreased.

Fluid circulation probably can be increased at the same power consumption and viscosity in laminar flow by increasing impeller diameter and decreasing rotational speed, but the relationship between Q, N, and D_a for laminar flow from turbines has not been determined.

As in the case of turbulent flow, then, small-diameter impellers ($D_a < D_T/3$) are useful for (1) rapid mixing of dry particles into liquids, (2) gas dispersion in slurries, (3) solid-particle deagglomeration, and (4) promoting mass transfer between solid and liquid phases. If stagnant regions are a problem, large impellers must be used and rotational speed and power increased to obtain the required results. Small continuous-processing equipment may be more economical than batch equipment in such cases.

Likewise, large-diameter impellers ($D_a > D_T/2$) are useful for (1) avoiding stagnant regions in slurries, (2) short mixing times to obtain uniformity throughout a vessel, (3) promotion of heat transfer, and (4) laminar continuous averaging of slurries.

Vortex Depth In an unbaffled vessel with an impeller rotating in the center, centrifugal force acting on the fluid raises the fluid level at the wall and lowers the level at the shaft. The depth and shape of such a vortex (Rieger, Ditl, and Novak, *Chem. Eng. Sci.*, **34,** 397 (1978)] depend on impeller and vessel dimensions as well as rotational speed.

Power Consumption of Impellers Power consumption is related to fluid density, fluid viscosity, rotational speed, and impeller diameter by plots of power number ($g_c P/\rho N^3 D_a^5$) versus Reynolds number ($D_a^2 N\rho/\mu$). Typical correlation lines for frequently used impellers operating in newtonian liquids contained in baffled cylindrical vessels are presented in Fig. 18-17. These curves may be used also for operation of the respective impellers in unbaffled tanks when the Reynolds number is 300 or less. When N_{Re} is greater than 300, however, the power consumption is lower in an unbaffled vessel than indicated in Fig. 18-17. For example, for a six-blade disk turbine with $D_T/D_a = 3$ and $D_a/W_i = 5$, $N_p = 1.2$ when $N_{Re} = 10^4$. This is only about one-fifth of the value of N_p when baffles are present.

Additional power data for other impeller types such as anchors, curved-blade turbines, and paddles in baffled and unbaffled vessels are available in the following references: Holland and Chapman, op. cit., chaps. 2, 4, Reinhold, New York, 1966; and Bates, Fondy, and Fenic, in Uhl and Gray, op. cit., vol. 1, chap. 3.

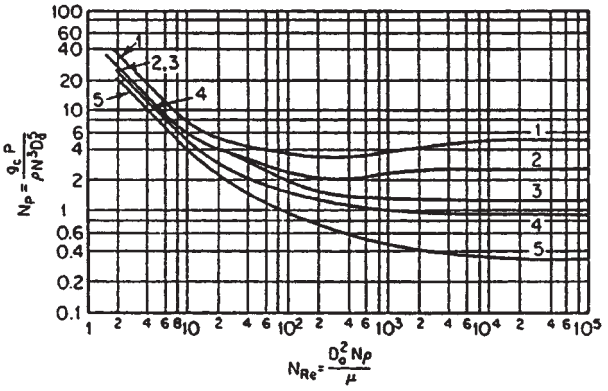


FIG. 18-17 Impeller power correlations: curve 1, six-blade turbine, $D_a/W_i = 5$, like Fig. 18-4 but with six blades, four baffles, each $D_T/12$; curve 2, vertical-blade, open turbine with six straight blades, $D_a/W_i = 8$, four baffles each $D_T/12$; curve 3, 45° pitched-blade turbine like Fig. 18-3 but with six blades, $D_a/W_i = 8$, four baffles, each $D_T/12$; curve 4, propeller, pitch equal to $2D_a$, four baffles, each $0.1D_T$, also same propeller in angular off-center position with no baffles; curve 5, propeller, pitch equal to D_a, four baffles each $0.1D_T$, also same propeller in angular off-center position as in Fig. 18-14 with no baffles. D_a = impeller diameter, D_T = tank diameter, g_c = gravitational conversion factor, N = impeller rotational speed, P = power transmitted by impeller shaft, W_i = impeller blade height, μ = viscosity of stirred liquid, and ρ = density of stirred mixture. Any set of consistent units may be used, but N must be rotations (rather than radians) per unit time. In the SI system, g_c is dimensionless and unity. [Curves 4 and 5 from Rushton, Costich, and Everett, *Chem. Eng. Prog.*, **46,** 395, 467 (1950), by permission; curves 2 and 3 from Bates, Fondy, and Corpstein, *Ind. Eng. Chem. Process Des. Dev.*, **2,** 310 (1963), by permission of the copyright owner, the American Chemical Society.]

Power consumption for impellers in pseudoplastic, Bingham plastic, and dilatant nonnewtonian fluids may be calculated by using the correlating lines of Fig. 18-17 if viscosity is obtained from viscosity-shear rate curves as described here. For a pseudoplastic fluid, viscosity decreases as shear rate increases. A Bingham plastic is similar to a pseudoplastic fluid but requires that a minimum shear stress be exceeded for any flow to occur. For a dilatant fluid, viscosity increases as shear rate increases.

The appropriate shear rate to use in calculating viscosity is given by one of the following equations when a propeller or a turbine is used (Bates et al., in Uhl and Gray, op. cit., vol. 1, p. 149):

For dilatant liquids,

$$\dot{\gamma} = 13N\left(\frac{D_a}{D_T}\right)^{0.5} \tag{18-6}$$

For pseudoplastic and Bingham plastic fluids,

$$\dot{\gamma} = 10N \tag{18-7}$$

where $\dot{\gamma}$ = average shear rate, s^{-1}.

The shear rate calculated from impeller rotational speed is used to identify a viscosity from a plot of viscosity versus shear rate determined with a capillary or rotational viscometer. Next N_{Re} is calculated, and N_p is read from a plot like Fig. 18-17.

DESIGN OF AGITATION EQUIPMENT

Selection of Equipment The principal factors which influence mixing-equipment choice are (1) the process requirements, (2) the flow properties of the process fluids, (3) equipment costs, and (4) construction materials required.

Ideally, the equipment chosen should be that of the lowest total cost which meets all process requirements. The total cost includes depreciation on investment, operating cost such as power, and maintenance costs. Rarely is any more than a superficial evaluation based on this

principle justified, however, because the cost of such an evaluation often exceeds the potential savings that can be realized. Usually optimization is based on experience with similar mixing operations. Often the process requirements can be matched with those of a similar operation, but sometimes tests are necessary to identify a satisfactory design and to find the minimum rotational speed and power.

There are no satisfactory specific guides for selecting mixing equipment because the ranges of application of the various types of equipment overlap and the effects of flow properties on process performance have not been adequately defined. Nevertheless, what is frequently done in selecting equipment is described in the following paragraphs.

Top-Entering Impellers For vessels less than 1.8 m (6 ft) in diameter, a clamp- or flange-mounted, angular, off-center fluidfoil impeller with no baffles should be the initial choice for meeting a wide range of process requirements (Fig. 18-14). The vessel straight-side-height-to-diameter ratio should be 0.75 to 1.5, and the volume of stirred liquid should not exceed 4 m^3 (about 1000 gal).

For suspension of free-settling particles, circulation of pseudoplastic slurries, and heat transfer or mixing of miscible liquids to obtain uniformity, a speed of 350 or 420 r/min should be stipulated. For dispersion of dry particles in liquids or for rapid initial mixing of liquid reactants in a vessel, an 1150- or 1750- r/min propeller should be used at a distance $D_T/4$ above the vessel bottom. A second propeller can be added to the shaft at a depth D_a below the liquid surface if the submergence of floating liquids or particulate solids is otherwise inadequate. Such propeller mixers are readily available up to 2.2 kW (3 hp) for off-center sloped-shaft mounting.

Propeller size, pitch, and rotational speed may be selected by model tests, by experience with similar operations, or, in a few cases, by published correlations of performance data such as mixing time or heat transfer. The propeller diameter and motor power should be the minimum which meet process requirements.

If agitation is required for a vessel less than 1.8 m (6 ft) in diameter and the same operations will be scaled up to a larger vessel ultimately, the equipment type should be the same as that expected in the larger vessel.

Axial-Flow Fluidfoil Impellers For vessel volumes of 4 to 200 m^3 (1000 to 50,000 gal), a turbine mixer mounted coaxially within the vessel with four or more baffles should be the initial choice. Here also the vessel straight-side-height-to-diameter ratio should be 0.75 to 1.5. Four vertical baffles should be fastened perpendicularly to the vessel wall with a gap between baffle and wall equal to $D_T/24$ and a radial baffle width equal to $D_T/12$.

For suspension of rapidly settling particles, the impeller turbine diameter should be $D_T/3$ to $D_T/2$. A clearance of less than one-seventh of the fluid depth in the vessel should be used between the lower edge of the turbine blade tips and the vessel bottom. As the viscosity of a suspension increases, the impeller diameter should be increased. This diameter may be increased to 0.6 D_T and a second impeller added to avoid stagnant regions in pseudoplastic slurries. Moving the baffles halfway between the impeller periphery and the vessel wall will also help avoid stagnant fluid near the baffles.

As has been shown, power consumption is decreased and turbine discharge rate is increased as impeller diameter is increased at constant torque (in the completely turbulent regime). This means that for a stipulated discharge rate, more efficient operation is obtained (lower power and torque) with a relatively large impeller operating at a relatively low speed ($N \propto D_a^{-3}$). Conversely, if power is held constant, decreasing impeller diameter results in increasing peripheral velocity and decreasing torque. Thus at a stipulated power level the rapid, efficient initial mixing of reactants identified with high peripheral velocity can be achieved by a relatively small impeller operating at a relatively high speed ($N \propto D_a^{-5/3}$).

For circulation and mixing to obtain uniformity, the impeller should be located at one-third of the liquid depth above the vessel bottom unless rapidly settling material or a need to stir a nearly empty vessel requires a lower impeller location.

Side-Entering Impellers For vessels greater than 4 m^3 (1000 gal), a side-entering propeller agitator (Fig. 18-9) may be more economical than a top-mounted impeller on a centered vertical shaft. For vessels greater than 38 m^3 (10,000 gal), the economic attractiveness of side-entering impellers increases. For vessels larger than 380 m^3 (100,000 gal), units may be as large as 56 kW (75 hp), and two or even three may be installed in one tank. For the suspension of slow-settling particles or the maintenance of uniformity in a viscous slurry of small particles, the diameter and rotational speed of a side-entering agitator must be selected on the basis of model tests or experience with similar operations.

When abrasive solid particles must be suspended, maintenance costs for the submerged shaft seal of a side-entering propeller may become high enough to make this type of mixer an uneconomical choice.

Jet Mixers Continuous recycle of the contents of a tank through an external pump so arranged that the pump discharge stream appropriately reenters the vessel can result in a flow pattern in the tank which will produce a slow mixing action [Fossett, *Trans. Inst. Chem. Eng.*, **29,** 322 (1951)].

Large Tanks Most large vessels (over 4 m^3) require a heavy-duty drive. About two-thirds of the mixing requirements industrially involve flow, circulation, and other types of pumping capacity requirements, including such applications as blending and solid suspension. There often is no requirement for any marked level of shear rate, so the use of the fluidfoil impellers is most common. If additional shear rate is required over what can be provided by the fluidfoil impeller, the axial-flow turbine (Fig. 18-3) is often used, and if extremely high shear rates are required, the flat-blade turbine (Rushton turbine) (Fig. 18-4) is required. For still higher shear rates, there is an entire variety of high-shear-rate impellers, typified by that shown in Fig. 18-10 that are used.

The fluidfoil impellers in large tanks require only two baffles, but three are usually used to provide better flow pattern asymmetry. These fluidfoil impellers provide a true axial flow pattern, almost as though there was a draft tube around the impeller. Two or three or more impellers are used if tanks with high D/T ratios are involved. The fluidfoil impellers do not vortex vigorously even at relatively low coverage so that if gases or solids are to be incorporated at the surface, the axial-flow turbine is often required and can be used in combination with the fluidfoil impellers also on the same shaft.

BLENDING

If the blending process is between two or more fluids with relatively low viscosity such that the blending is not affected by fluid shear rates, then the difference in blend time and circulation between small and large tanks is the only factor involved. However, if the blending involves wide disparities in the density of viscosity and surface tension between the various phases, then a certain level of shear rate may be required before blending can proceed to the required degree of uniformity.

The role of viscosity is a major factor in going from the turbulent regime, through the transition region, into the viscous regime and the change in the role of energy dissipation discussed previously. The role of non-newtonian viscosities comes into the picture very strongly since that tends to markedly change the type of influence of impellers and determines the appropriate geometry that is involved.

There is the possibility of misinterpretation of the difference between circulation time and blend time. Circulation time is primarily a function of the pumping capacity of the impeller. For axial-flow impellers, a convenient parameter, but not particularly physically accurate, is to divide the pumping capacity of the impeller by the cross-sectional area of the tank to give a superficial liquid velocity. This is sometimes used by using the total volume of flow from the impeller including entrainment of the tank to obtain a superficial liquid velocity.

As the flow from an impeller is increased from a given power level, there will be a higher fluid velocity and therefore a shorter circulation time. This holds true when dealing with any given impeller. This is shown in Fig. 18-18, which shows that circulation time versus D/T decreases. A major consideration is when increasing D/T becomes too large and actually causes the curve to reverse. This occurs somewhere around 0.45, ± 0.05, so that using impellers of D/T ratios of 0.6 to 0.8

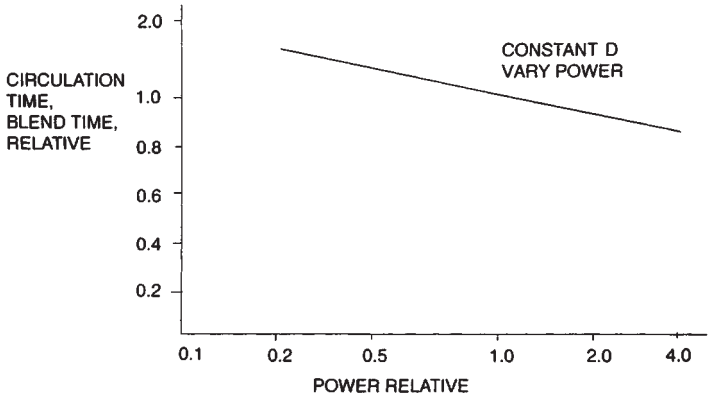


FIG. 18-18 Effect of *D/T* ratio on two different impellers on the circulation time and the blend time.

is often counterproductive for circulation time. They may be useful for the blending or motion of pseudoplastic fluids.

When comparing different impeller types, an entirely different phenomenon is important. In terms of circulation time, the phenomena shown in Figs. 18-18 and 18-19 still apply with the different impellers shown in Fig. 18-5. When it comes to blending another factor enters the picture. When particles A and B meet each other as a result of shear rates, there has to be sufficient shear stress to cause A and B to blend, react, or otherwise participate in the process.

It turns out that in low-viscosity blending the actual result does depend upon the measuring technique used to measure blend time. Two common techniques, which do not exhaust the possibilities in reported studies, are to use an acid-base indicator and inject an acid or base into the system that will result in a color change. One can also put a dye into the tank and measure the time for color to arrive at uniformity. Another system is to put in a conductivity probe and inject a salt or other electrolyte into the system. With any given impeller type at constant power, the circulation time will increase with the *D/T* ratio of the impeller. Figure 18-18 shows that both circulation time and blend time decrease as *D/T* increases. The same is true for impeller speed. As impeller speed is increased with any impeller, blend time and circulation time are decreased (Fig. 18-19).

However, when comparing different impeller types at the same power level, it turns out that impellers that have a higher pumping capacity will give decreased circulation time, but all the impellers, regardless of their pumping efficiency, give the same blend time at the same power level and same diameter. This means that circulation time must be combined with shear rate to carry out a blending experiment which involves chemical reactions or interparticle mixing (Fig. 18-20).

For other situations in low-viscosity blending, the fluid in tanks may become stratified. There are few studies on that situation, but Oldshue (op. cit.) indicates the relationship between some of the variables. The important difference is that blend time is inversely proportional to power, not impeller flow, so that the exponents are quite different for a stratified tank. This situation occurs more frequently in the petroleum industry, where large petroleum storage tanks become stratified either by filling techniques or by temperature fluctuations.

There is a lot of common usage of the terms *blend time, mixing time,* and *circulation time.* There are differences in concept and interpretation of these different "times." For any given experiment, one must pick a definition of *blend time* to be used. As an example, if one is measuring the fluctuation of concentration after an addition of material to the tank, then one can pick an arbitrary definition of blending such as reducing the fluctuations below a certain level. This often is chosen as a fluctuation equal to 5% of the original fluctuation when the feed material is added. This obviously is a function of the size of the probe used to measure these fluctuations, which often is on the order of 500 to 1000 μm.

At the micro-scale level, there really is no way to measure concentration fluctuations. Resort must be made to other qualitative interpretation of results for either a process or a chemical reaction study.

High-Viscosity Systems All axial-flow impellers become radial flow as Reynolds numbers approach the viscous region. Blending in

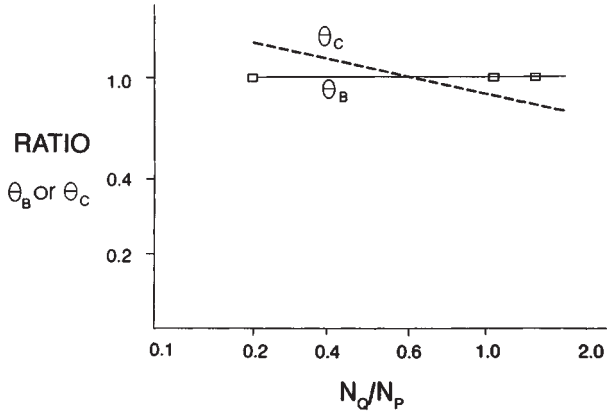


FIG. 18-19 Effect of impeller speed and power for the same diameter on circulation time and blend time for a particular impeller.

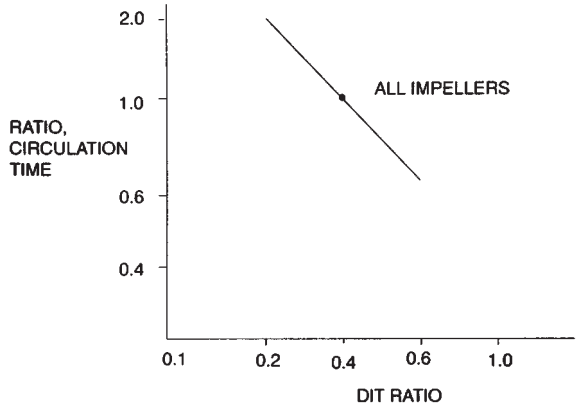


FIG. 18-20 At constant power and constant impeller diameter, three different impellers give the same blend time but different circulation times.

the transition and low-viscosity system is largely a measure of fluid motion throughout the tank. For close-clearance impellers, the anchor and helical impellers provide blending by having an effective action at the tank wall, which is particularly suitable for pseudoplastic fluids.

Figure 18-21 gives some data on the circulation time of the helical impeller. It has been observed that it takes about three circulation times to get one blend time being the visual uniformity of a dye added to the material. This is a macro-scale blending definition.

Axial-flow turbines are often used in blending pseudoplastic materials, and they are often used at relatively large D/T ratios, from 0.5 to 0.7, to adequately provide shear rate in the majority of the batch particularly in pseudoplastic material. These impellers develop a flow pattern which may or may not encompass an entire tank, and these areas of motion are sometimes referred to as *caverns.* Several papers describe the size of these caverns relative to various types of mixing phenomena. An effective procedure for the blending of pseudoplastic fluids is given in Oldshue (op. cit.).

Chemical Reactions Chemical reactions are influenced by the uniformity of concentration both at the feed point and in the rest of the tank and can be markedly affected by the change in overall blend time and circulation time as well as the micro-scale environment. It is possible to keep the ratio between the power per unit volume at the impeller and in the rest of the tank relatively similar on scale-up, but many details need to be considered when talking about the reaction conditions, particularly where they involve selectivity. This means that reactions can take different paths depending upon chemistry and fluid mechanics, which is a major consideration in what should be examined. The method of introducing the reagent stream can be projected in several different ways depending upon the geometry of the impeller and feed system.

Chemical reactions normally occur in the micro-scale range. In turbulent flow, almost all of the power dissipation occurs eventually in the micro-scale regime because that is the only place where the scale of the fluid fluctuations is small enough that viscous shear stress exists. At approximately 100 μm, the fluid does not know what type of impeller is used to generate the power; continuing down to 10 μm and, even further, to chemical reactions, the actual impeller type is not a major variable as long as the proper macro-scale regime has been provided throughout the entire tank. The intensity of the mixing environment in the micro-scale regime can be related to a series of variables in an increasing order of complexity. Since all of the power is ultimately dissipated in the micro-scale regime, the power per unit volume throughout the tank is one measure of the overall measure of micro-scale mixing and the power dissipation at individual volumes in the tank is another way of expressing the influence. In general, the power per unit volume dissipated around an impeller zone can be 100 times higher than the power dissipated throughout the remainder of the tank.

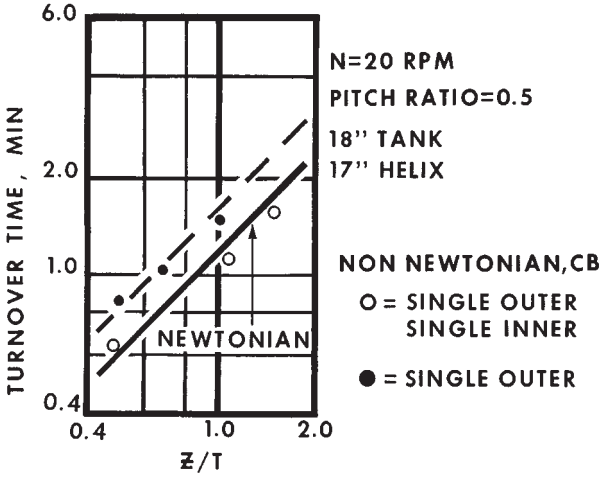


FIG. 18-21 Effect of impeller speed on circulation time for a helical impeller in the Reynolds number arranged less than 10.

The next level of complexity is to look at the rms velocity fluctuation, which is typically 50 percent of the mean velocity around the impeller zone and about 5 percent of the mean velocity in the rest of the vessel. This means that the feed introduction point for either a single reactant or several reactants can be of extreme importance. It seems that the selectivity of competing or consecutive chemical reactions can be a function of the rms velocity fluctuations in the feed point if the chemical reactants remain constant and involve an appropriate relationship to the time between the rms velocity fluctuations. There are three common ways of introducing reagents into a mixing vessel. One is to let them drip on the surface. The second is to use some type of introduction pipe to bring the material into various parts of the vessel. The third is to purposely bring them in and around the impeller zone. Generally, all three methods have to be tried before determining the effect of feed location.

Since chemical reactions are on a scale much below 1 μm, and it appears that the Komolgoroff scale of isotropic turbulence turns out to be somewhere between 10 and 30 μm, other mechanisms must play a role in getting materials in and out of reaction zones and reactants in and out of those zones. One cannot really assign a shear rate magnitude to the area around a micro-scale zone, and it is primarily an environment that particles and reactants witness in this area.

The next level of complexity looks at the kinetic energy of turbulence. There are several models that are used to study the fluid mechanics, such as the Kε model. One can also put the velocity measurements through a spectrum analyzer to look at the energy at various wave numbers.

In the viscous regime, chemical reactants become associated with each other through viscous shear stresses. These shear stresses exist at all scales (macro to micro) and until the power is dissipated continuously through the entire spectrum. This gives a different relationship for power dissipation than in the case of turbulent flow.

Solid-Liquid The most-used technique to study solid suspension, as documented in hundreds of papers in the literature, is called the *speed for just suspension,* N_{JS}. The original work was done in 1958 by Zwietering and this is still the most extensive range of variables, although other investigators have added to it considerably.

This particular technique is suitable only for laboratory investigation using tanks that are transparent and well illuminated. It does not lend itself to evaluation of the opaque tanks, nor is it used in any study of large-scale tanks in the field. It is a very minimal requirement for uniformity, and definitions suggested earlier are recommended for use in industrial design.

Some Observations on the Use of $\mathbf{N_{JS}}$ With D/T ratios of less than 0.4, uniformity throughout the rest of the tank is minimal. In D/T ratios greater than 0.4, the rest of the tank has a very vigorous fluid motion with marked approach to complete uniformity before N_{JS} is reached.

Much of the variation in N_{JS} can be reduced by using P_{JS}, which is the power in the just-suspended state. This also gives a better feel for the comparison of various impellers based on the energy requirement rather than speed, which has no economic relevance.

The overall superficial fluid velocity, mentioned earlier, should be proportional to the settling velocity of the solids if that were the main mechanism for solid suspension. If this were the case, the requirement for power if the settling velocity were doubled should be eight times. Experimentally, it is found that the increase in power is more nearly four times, so that some effect of the shear rate in macro-scale turbulence is effective in providing uplift and motion in the system.

Picking up the solids at the bottom of the tank depends upon the eddies and velocity fluctuations in the lower part of the tank and is a different criterion from the flow pattern required to keep particles suspended and moving in various velocity patterns throughout the remainder of the vessel. This leads to the variables in the design equation and a relationship that is quite different when these same variables are studied in relation to complete uniformity throughout the mixing vessel.

Another concern is the effect of multiple particle sizes. In general, the presence of fine particles will affect the requirements of suspen-

sion of larger particles. The fine particles act largely as a potential viscosity-increasing agent and give a similar result to what would happen if the viscosity of the continuous phase were increased.

Another phenomenon is the increase in power required with percent solids, which makes a dramatic change at approximately 40 percent by volume, and then dramatically changes again as we approach the ultimate weight percent of settled solids. This phenomenon is covered by Oldshue (op. cit.), who describes conditions required for mixing slurries in the 80 to 100 percent range of the ultimate weight percent of settled solids.

Solids suspension in general is not usually affected by blend time or shear-rate changes in the relatively low to medium solids concentration in the range from 0 to 40 percent by weight. However, as solids become more concentrated, the effect of solids concentration on power required gives a change in criterion from the settling velocity of the individual particles in the mixture to the apparent viscosity of the more concentrated slurry. This means that we enter into an area where the blending of non-newtonian fluid regions affects the shear rates and plays a marked role.

The suspension of a single solid particle should depend primarily on the upward velocity at a given point and also should be affected by the uniformity of this velocity profile across the entire tank cross section. There are upward velocities in the tank and there also must be corresponding downward velocities.

In addition to the effect of the upward velocity on a settling particle, there is also the random motion of the micro-scale environment, which does not affect large particles very much but is a major factor in the concentration and uniformity of particles in the transition and micro-scale size range.

Using a draft tube in the tank for solids suspension introduces another, different set of variables. There are other relationships that are very much affected by scale-up in this type of process, as shown in Fig. 18-22. Different scale-up problems exist whether the impeller is pumping up or down within the draft tube.

Solid Dispersion If the process involves the dispersion of solids in a liquid, then we may either be involved with breaking up agglomerates or possibly physically breaking or shattering particles that have a low cohesive force between their components. Normally, we do not think of breaking up ionic bonds with the shear rates available in mixing machinery.

If we know the shear stress required to break up a particle, we can then determine the shear rate required from the machinery by various viscosities with the equation:

$$\text{Shear stress} = \text{viscosity (shear rate)}$$

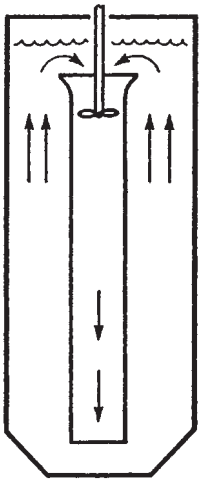


FIG. 18-22 Typical draft tube circulator, shown here for down-pumping mode for the impeller in the draft tube.

The shear rate available from various types of mixing and dispersion devices is known approximately and also the range of viscosities in which they can operate. This makes the selection of the mixing equipment subject to calculation of the shear stress required for the viscosity to be used.

In the equation referred to above, it is assumed that there is 100 percent transmission of the shear rate in the shear stress. However, with the slurry viscosity determined essentially by the properties of the slurry, at high concentrations of slurries there is a slippage factor. Internal motion of particles in the fluids over and around each other can reduce the effective transmission of viscosity efficiencies from 100 percent to as low as 30 percent.

Animal cells in biotechnology do not normally have tough skins like those of fungal cells and they are very sensitive to mixing effects. Many approaches have been and are being tried to minimize the effect of increased shear rates on scale-up. These include encapsulating the organism in or on microparticles and/or conditioning cells selectively to shear rates. In addition, traditional fermentation processes have maximum shear-rate requirements in which cells become progressively more and more damaged until they become motile.

Solid-Liquid Mass Transfer There is potentially a major effect of both shear rate and circulation time in these processes. The solids can either be fragile or rugged. We are looking at the slip velocity of the particle and also whether we can break up agglomerates of particles which may enhance the mass transfer. When the particles become small enough, they tend to follow the flow pattern, so the slip velocity necessary to affect the mass transfer becomes less and less available.

What this shows is that, from the definition of off-bottom motion to complete uniformity, the effect of mixer power is much less than from going to on-bottom motion to off-bottom suspension. The initial increase in power causes more and more solids to be in active communication with the liquid and has a much greater mass-transfer rate than that occurring above the power level for off-bottom suspension, in which slip velocity between the particles of fluid is the major contributor (Fig. 18-23).

Since there may well be chemical or biological reactions happening on or in the solid phase, depending upon the size of the process participants, macro- or micro-scale effects may or may not be appropriate to consider.

In the case of living organisms, their access to dissolved oxygen throughout the tank is of great concern. Large tanks in the fermentation industry often have a Z/T ratio of 2:1 to 4:1; thus, top-to-bottom blending can be a major factor. Some biological particles are facultative and can adapt and reestablish their metabolisms at different dissolved-oxygen levels. Other organisms are irreversibly destroyed by sufficient exposure to low dissolved-oxygen levels.

GAS-LIQUID SYSTEMS

Gas-Liquid Dispersion This involves physical dispersion of gas bubbles by the impeller, and the effect of gas flow on the impeller.

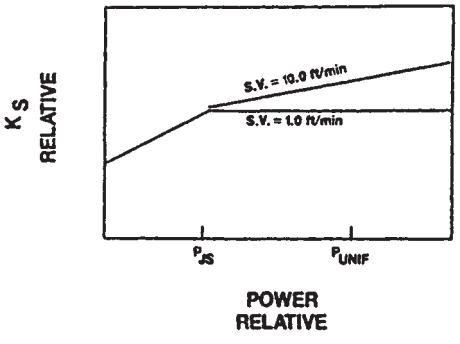


FIG. 18-23 Relative change in solid-liquid mass-transfer ratio with three different suspension levels, i.e., on-bottom motion, off-bottom motion, and complete uniformity.

The observation of the physical appearance of a tank undergoing gas-liquid mass transfer can be helpful but is not a substitute for mass-transfer data on the actual process. The mixing vessel can have four regimes of visual comparisons between gas bubbles and flow patterns. A helpful parameter is the ratio between the power given up by the gas phase and the power introduced by the mixing impeller. In general, if the power in the gas stream (calculated as the expansion energy from the gas expanding from the sparging area to the top of the tank, shown in Fig. 18-24) is greater, there will be considerable blurping and entrainment of liquid drops by a very violent explosion of gas bubbles at the surface. If the power level is more than the expanding gas energy, then the surface action will normally be very coalescent and uniform by comparison, and the gas will be reasonably well distributed throughout the remainder of the tank. With power levels up to 10 to 100 times the gas energy, the impeller will cause a more uniform and vigorous dispersion of the gas bubbles and smaller gas bubbles in the vessel.

In the 1960s and before, most gas-liquid operations were conducted using flat-blade turbines as shown in Fig. 18-4. These impellers required input of approximately three times the energy in the gas stream before they completely control the flow pattern. This was usually the case, and the mass-transfer characteristics were comparable to what would be expected. One disadvantage of the radial-flow impeller is that it is a very poor blending device so blend time is very long compared to that in pilot-scale experiments and compared to the fluidfoil impeller types often used currently. Using curvature of the blades to modify the tendency of gas bubbles to streamline the back of the flat-blade turbine gives a different characteristic to the power drawn by the impeller at a given gas rate compared to no gas rate, but it seems to give quite similar mass transfer at power levels similar to those of the flat-blade design. In order to improve the blending and solid-suspension characteristics, fluidfoil impellers (typified by the A315, Fig. 18-25) have been introduced in recent years and they have many of the advantages and some of the disadvantages of the flat-blade turbine. These impellers typically have a very high solidity ratio, on the order of 0.85 or more, and produce a strong axial downflow at low gas rate. As the gas rate increases, the flow pattern becomes more radial due to the upflow of the gas counteracting the downward flow of the impeller.

Mass-transfer characteristics on large-scale equipment seem to be quite similar, but the fluidfoil impellers tend to release a larger-diameter bubble than is common with the radial-flow turbines. The blend time is one-half or one-third as long, and solid-suspension characteristics are better so that there have been notable improved process results with these impellers. This is particularly true if the process requires better blending and there is solid suspension. If this is not the case, the results from these impellers can be negative compared to radial-flow turbines.

It is very difficult to test these impellers on a small scale, since they provide better blending on a pilot scale where blending is already very effective compared to the large scale. Caution is recommended if it is desirable to study these impellers in pilot-scale equipment.

Gas-Liquid Mass Transfer Gas-liquid mass transfer normally is correlated by means of the mass-transfer coefficient $K_g a$ versus power level at various superficial gas velocities. The superficial gas velocity is the volume of gas at the average temperature and pressure at the midpoint in the tank divided by the area of the vessel. In order to obtain the partial-pressure driving force, an assumption must be made of the partial pressure in equilibrium with the concentration of gas in the liquid. Many times this must be assumed, but if Fig. 18-26 is obtained in the pilot plant and the same assumption principle is used in evaluating the mixer in the full-scale tank, the error from the assumption is limited.

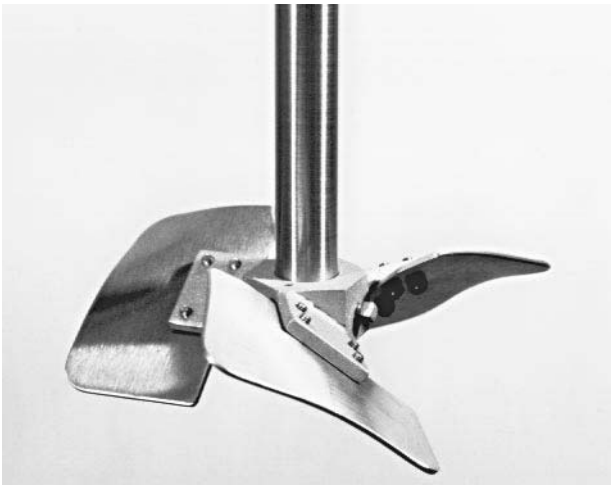


FIG. 18-25 An impeller designed for gas-liquid dispersion and mass transfer of the fluidfoil type, i.e., A315.

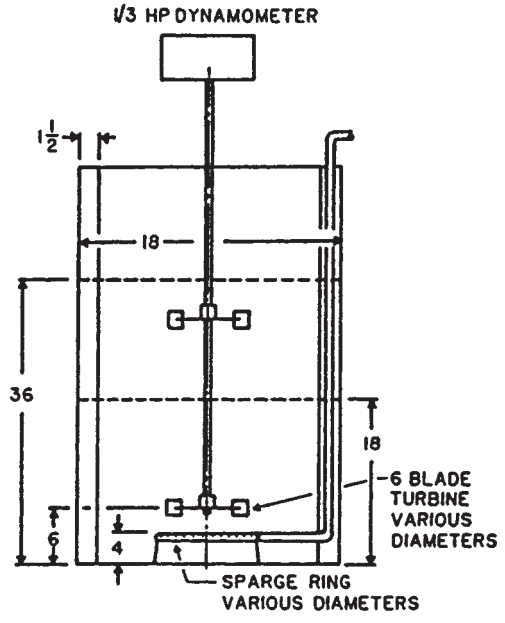


FIG. 18-24 Typical arrangement of Rushton radial-flow R100 flat-blade turbine with typical sparge ring for gas-liquid mass transfer.

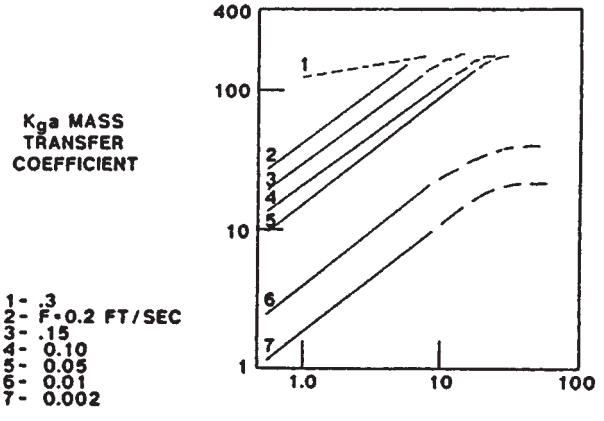


FIG. 18-26 Typical curve for mass transfer coefficient $K_g a$ as a function of mixer power and superficial gas velocity.

In the plant-size unit, Fig. 18-26 must be translated into a mass-transfer-rate curve for the particular tank volume and operating condition selected. Every time a new physical condition is selected, a different curve similar to that of Fig. 18-27 is obtained.

Typical exponents on the effect of power and gas rate on $K_g a$ tend to be around 0.5 for each variable, ± 0.1.

Viscosity markedly changes the picture and, usually, increasing viscosity lowers the mass-transfer coefficient. For the common application of waste treating and for some of the published data on biological slurries, data for $k_L a$ (shown in Fig. 18-28) is obtained in the literature. For a completely new gas or liquid of a liquid slurry system, Fig. 18-26 must be obtained by an actual experiment.

Liquid-Gas-Solid Systems Many gas-liquid systems contain solids that may be the ultimate recipient of the liquid-gas-solid mass transfer entering into the process result. Examples are biological processes in which the biological solids are the user of the mass transfer of the mixing-flow patterns, various types of slurries reactors in which the solids either are being reactive or there may be extraction or dissolving taking place, or there may be polymerization or precipitation of solids occurring.

Normally there must be a way of determining whether the mass-transfer rate with the solids is the key controlling parameter or the gas-liquid mass transfer rate.

In general, introduction of a gas stream to a fluid will increase the blend time because the gas-flow patterns are counterproductive to the typical mixer-flow patterns. In a similar vein, the introduction of a gas stream to a liquid-solid suspension will decrease the suspension uniformity because the gas-flow pattern is normally counterproductive to the mixer-flow pattern. Many times the power needed for the gas-liquid mass transfer is higher than the power needed for solid suspension, and the effect of the gas flow on the solid suspensions are of little concern. On the other hand, if power levels are relatively low and solid-suspension characteristics are critical—examples being the case of activated sludge reactors in the waste-treating field or biological solid reactors in the hydrometallurgical field—then the effect of the gas-flow pattern of the mixing system can be quite critical to the overall design.

Another common situation is batch hydrogenation, in which pure hydrogen is introduced to a relatively high pressure reactor and a decision must be made to recycle the unabsorbed gas stream from the top of the reactor or use a vortexing mode for an upper impeller to incorporate the gas from the surface.

Loop Reactors For some gas-liquid-solid processes, a recirculating loop can be an effective reactor. These involve a relatively high horsepower pumping system and various kinds of nozzles, baffles, and turbulence generators in the loop system. These have power levels anywhere from 1 to 10 times higher than the power level in a typical mixing reactor, and may allow the retention time to be less by a factor of 1 to 10.

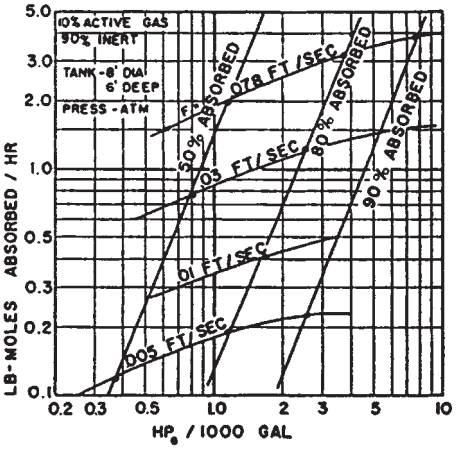


FIG. 18-27 Example of a specific chart to analyze the total mass-transfer rate in a particular tank under a process condition obtained from basic $K_g a$ data shown in Fig. 18-25.

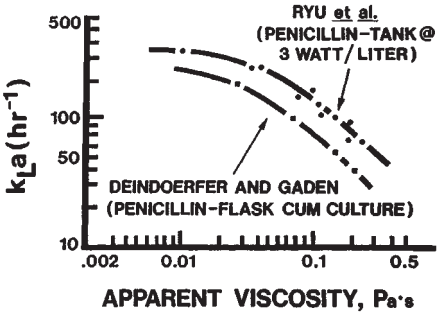


FIG. 18-28 Usually, the gas-liquid mass-transfer coefficient, $K_g a$, is reduced with increased viscosity. This shows the effect of increased concentration of microbial cells in a fermentation process.

LIQUID-LIQUID CONTACTING

Emulsions Almost every shear rate parameter affects liquid-liquid emulsion formation. Some of the effects are dependent upon whether the emulsion is both dispersing and coalescing in the tank, or whether there are sufficient stabilizers present to maintain the smallest droplet size produced for long periods of time. Blend time and the standard deviation of circulation times affect the length of time it takes for a particle to be exposed to the various levels of shear work and thus the time it takes to achieve the ultimate small particle size desired.

The prediction of drop sizes in liquid-liquid systems is difficult. Most of the studies have used very pure fluids as two of the immiscible liquids, and in industrial practice there almost always are other chemicals that are surface-active to some degree and make the prediction of absolute drop sizes very difficult. In addition, techniques to measure drop sizes in experimental studies have all types of experimental and interpretation variations and difficulties so that many of the equations and correlations in the literature give contradictory results under similar conditions. Experimental difficulties include dispersion and coalescence effects, difficulty of measuring actual drop size, the effect of visual or photographic studies on where in the tank you can make these observations, and the difficulty of using probes that measure bubble size or bubble area by light or other sample transmission techniques which are very sensitive to the concentration of the dispersed phase and often are used in very dilute solutions.

It is seldom possible to specify an initial mixer design requirement for an absolute bubble size prediction, particularly if coalescence and dispersion are involved. However, if data are available on the actual system, then many of these correlations could be used to predict relative changes in drop size conditions with changes in fluid properties or impeller variables.

STAGEWISE EQUIPMENT: MIXER-SETTLERS

Introduction Insoluble liquids may be brought into direct contact to cause transfer of dissolved substances, to allow transfer of heat, and to promote chemical reaction. This subsection concerns the design and selection of equipment used for conducting this type of liquid-liquid contact operation.

Objectives There are four principal purposes of operations involving the direct contact of immiscible liquids. The purpose of a particular contact operation may involve any one or any combination of the following objectives:

1. *Separation of components in solution.* This includes the ordinary objectives of liquid extraction, in which the constituents of a solution are separated by causing their unequal distribution between two insoluble liquids, the washing of a liquid with another to remove small

amounts of a dissolved impurity, and the like. The theoretical principles governing the phase relationships, material balances, and number of ideal stages or transfer units required to bring about the desired changes are to be found in Sec. 15. Design of equipment is based on the quantities of liquids and the efficiency and operating characteristics of the type of equipment selected.

2. *Chemical reaction.* The reactants may be the liquids themselves, or they may be dissolved in the insoluble liquids. The kinetics of this type of reaction are treated in Sec. 4.

3. *Cooling or heating a liquid by direct contact with another.* Although liquid-liquid-contact operations have not been used widely for heat transfer alone, this technique is one of increasing interest. Applications also include cases in which chemical reaction or liquid extraction occurs simultaneously.

4. *Creating permanent emulsions.* The objective is to disperse one liquid within another in such finely divided form that separation by settling either does not occur or occurs extremely slowly. The purpose is to prepare the emulsion. Neither extraction nor chemical reaction between the liquids is ordinarily sought.

Liquid-liquid contacting equipment may be generally classified into two categories: **stagewise** and **continuous** (**differential**) contact.

The function of a stage is to contact the liquids, allow equilibrium to be approached, and to make a mechanical separation of the liquids. The contacting and separating correspond to mixing the liquids, and settling the resulting dispersion; so these devices are usually called **mixer-settlers.** The operation may be carried out in batch fashion or with continuous flow. If batch, it is likely that the same vessel will serve for both mixing and settling, whereas if continuous, separate vessels are usually but not always used.

Mixer-Settler Equipment The equipment for extraction or chemical reaction may be classified as follows:

I. Mixers
  A. Flow or line mixers
    1. Mechanical agitation
    2. No mechanical agitation
  B. Agitated vessels
    1. Mechanical agitation
    2. Gas agitation
II. Settlers
  A. Nonmechanical
    1. Gravity
    2. Centrifugal (cyclones)
  B. Mechanical (centrifuges)
  C. Settler auxiliaries
    1. Coalescers
    2. Separator membranes
    3. Electrostatic equipment

In principle, at least, any mixer may be coupled with any settler to provide the complete stage. There are several combinations which are especially popular. Continuously operated devices usually, but not always, place the mixing and settling functions in separate vessels. Batch-operated devices may use the same vessel alternately for the separate functions.

Flow or Line Mixers

Definition Flow or line mixers are devices through which the liquids to be contacted are passed, characterized principally by the very small time of contact for the liquids. They are used only for continuous operations or semibatch (in which one liquid flows continuously and the other is continuously recycled). If holding time is required for extraction or reaction, it must be provided by passing the mixed liquids through a vessel of the necessary volume. This may be a long pipe of large diameter, sometimes fitted with segmental baffles, but frequently the settler which follows the mixer serves. The energy for mixing and dispersing usually comes from pressure drop resulting from flow.

There are many types, and only the most important can be mentioned here. [See also Hunter, in Dunstan (ed.), *Science of Petroleum,* vol. 3, Oxford, New York, 1938, pp. 1779–1797.] They are used fairly extensively in treating petroleum distillates, in vegetable-oil, refining, in extraction of phenol-bearing coke-oven liquors, in some metal extractions, and the like. Kalichevsky and Kobe (*Petroleum Refining with Chemicals,* Elsevier, New York, 1956) discuss detailed application in the refining of petroleum.

Jet Mixers These depend upon impingement of one liquid on the other to obtain a dispersion, and one of the liquids is pumped through a small nozzle or orifice into a flowing stream of the other. Both liquids are pumped. They can be used successfully only for liquids of low interfacial tension. See Fig. 18-29 and also Hunter and Nash [*Ind. Chem.,* **9,** 245, 263, 317 (1933)]. Treybal (*Liquid Extraction,* 2d ed., McGraw-Hill, New York, 1963) describes a more elaborate device. For a study of the extraction of antibiotics with jet mixers, see Anneskova and Boiko, *Med. Prom. SSSR,* **13**(5), 26 (1959). Insonation with ultrasound of a toluene-water mixture during methanol extraction with a simple jet mixer improves the rate of mass transfer, but the energy requirements for significant improvement are large [Woodle and Vilbrandt, *Am. Inst. Chem. Eng. J.,* **6,** 296 (1960)].

Injectors The flow of one liquid is induced by the flow of the other, with only the majority liquid being pumped at relatively high velocity. Figure 18-30 shows a typical device used in semibatch fashion for washing oil with a recirculated wash liquid. It is installed directly in the settling drum. See also Hampton (U.S. Patent 2,091,709, 1933), Sheldon (U.S. Patent 2,009,347, 1935), and Ng (U.S. Patent 2,665,975, 1954). Folsom [*Chem. Eng. Prog.,* **44,** 765 (1948)] gives a good review of basic principles. The most thorough study for extraction is provided by Kafarov and Zhukovskaya [*Zh. Prikl. Khim.,* **31,** 376 (1958)], who used very small injectors. With an injector measuring 73 mm from throat to exit, with 2.48-mm throat diameter, they extracted benzoic acid and acetic acid from water with carbon tetrachloride at the rate of 58 to 106 L/h, to obtain a stage efficiency $E = 0.8$ to 1.0. Data on flow characteristics are also given. Boyadzhiev and Elenkov [*Collect. Czech. Chem. Commun.,* **31,** 4072 (1966)] point out that the presence of surface-active agents exerts a profound influence on drop size in such devices.

Orifices and Mixing Nozzles Both liquids are pumped through constrictions in a pipe, the pressure drop of which is partly utilized to create the dispersion (see Fig. 18-31). Single nozzles or several in series may be used. For the orifice mixers, as many as 20 orifice plates each with 13.8-kPa (2-lb/in^2) pressure drop may be used in series [Morell and Bergman, *Chem. Metall. Eng.,* **35,** 211 (1928)]. In the Dualayer process for removal of mercaptans from gasoline, 258 m^3/h (39,000 bbl/day) of oil and treating solution are contacted with 68.9-kPa (10-lb/in^2) pressure drop per stage [Greek et al., *Ind. Eng. Chem.,* **49,** 1938 (1957)]. Holland et al. [*Am. Inst. Chem. Eng. J.,* **4,** 346 (1958); **6,** 615 (1960)] report on the interfacial area produced between two immiscible liquids entering a pipe (diameter 0.8 to 2.0 in) from an orifice, $\gamma_D = 0.02$ to 0.20, at flow rates of 0.23 to 4.1 m^3/h (1 to 18 gal/min). At a distance 17.8 cm (7 in) downstream from the orifice,

$$a_{av} = \frac{0.179}{\sigma g_c} (C_O^2 \Delta p)^{0.75} \left(\frac{\sigma \sqrt{g_c \rho_{av}}}{\mu_D} \right)^{0.158} \left[\left(\frac{d_t}{d_O} \right)^4 - 1 \right]^{0.117} \gamma_D^{0.878} \quad (18\text{-}8)$$

where a_{av} = interfacial surface, cm^2/cm^3; C_O = orifice coefficient, dimensionless; d_t = pipe diameter, in; d_O = orifice diameter, in; g_c =

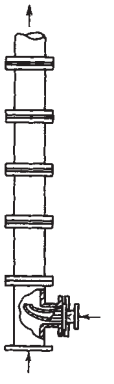


FIG. 18-29 Elbow jet mixer.

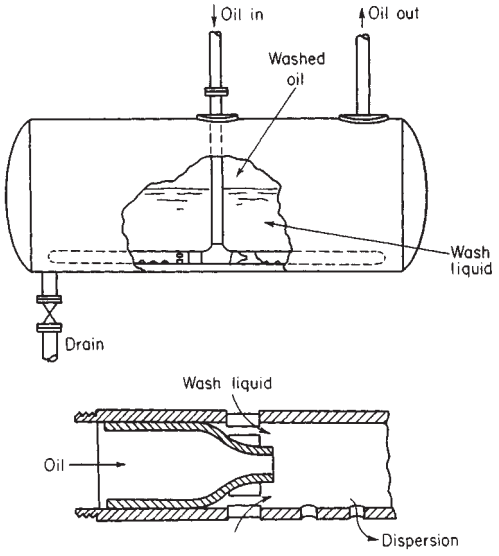


FIG. 18-30 Injector mixer. (*Ayres, U.S. Patent 2,531,547, 1950.*)

gravitational conversion factor, (32.2 lbm·ft)/(lbf·s^2); Δp = pressure drop across orifice, lbf/ft^2; μ_D = viscosity of dispersed phase, lbm/(ft·s); ρ_{av} = density of dispersed phase, lbm/ft; and σ = interfacial tension, lbf/ft. See also Shirotsuka et al. [*Kagaku Kogaku,* **25,** 109 (1961)].

Valves Valves may be considered to be adjustable orifice mixers. In desalting crude petroleum by mixing with water, Hayes et al. [*Chem. Eng. Prog.,* **45,** 235 (1949)] used a globe-valve mixer operating at 110- to 221-kPa (16- to 32-lb/in^2) pressure drop for mixing 66 m^3/h (416 bbl/h) oil with 8 m^3/h (50 bbl/h) water, with best results at the lowest value. Simkin and Olney [*Am. Inst. Chem. Eng. J.,* **2,** 545 (1956)] mixed kerosine and white oil with water, using 0.35- to 0.62-kPa (0.05- to 0.09-lb/in^2) pressure drop across a 1-in gate valve, at 22-m^3/h (10-gal/min) flow rate for optimum separating conditions in a cyclone, but higher pressure drops were required to give good extractor efficiencies.

Pumps Centrifugal pumps, in which the two liquids are fed to the suction side of the pump, have been used fairly extensively, and they offer the advantage of providing interstage pumping at the same time. They have been commonly used in the extraction of phenols from coke-oven liquors with light oil [Gollmar, *Ind. Eng. Chem.,* **39,** 596, 1947); Carbone, *Sewage Ind. Wastes,* **22,** 200 (1950)], but the intense shearing action causes emulsions with this low-interfacial-tension system. Modern plants use other types of extractors. Pumps are useful in the extraction of slurries, as in the extraction of uranyl nitrate from acid-uranium-ore slurries [*Chem. Eng.,* **66,** 30 (Nov. 2, 1959)]. Shaw and Long [*Chem. Eng.,* **64**(11), 251 (1957)] obtain a stage efficiency of 100 percent (E = 1.0) in a uranium-ore-slurry extraction with an open impeller pump. In order to avoid emulsification difficulties in these extractions, it is necessary to maintain the organic phase continuous, if necessary by recycling a portion of the settled organic liquid to the mixer.

Agitated Line Mixer See Fig. 18-32. This device, which combines the features of orifice mixers and agitators, is used extensively in treating petroleum and vegetable oils. It is available in sizes to fit ½- to 10-in pipe. The device of Fig. 18-33, with two impellers in separate stages, is available in sizes to fit 4- to 20-in pipe.

Packed Tubes Cocurrent flow of immiscible liquids through a packed tube produces a one-stage contact, characteristic of line mixers. For flow of isobutanol-water* through a 0.5-in diameter tube packed with 6 in of 3-mm glass beads, Leacock and Churchill [*Am. Inst. Chem. Eng. J.,* **7,** 196 (1961)] find

$$k_C a_{av} = c_1 L_C^{0.5} L_D \tag{18-9}$$

$$k_D a_{av} = c_2 L_C^{0.75} L_D^{0.75} \tag{18-10}$$

where c_1 = 0.00178 using SI units and 0.00032 using U.S. customary units; and c_2 = 0.0037 using SI units and 0.00057 using U.S. customary units. These indicate a stage efficiency approaching 100 percent. Organic-phase holdup and pressure drop for larger pipes similarly packed are also available [Rigg and Churchill, ibid., **10,** 810 (1964)].

Pipe Lines The principal interest here will be for flow in which one liquid is dispersed in another as they flow cocurrently through a pipe (stratified flow produces too little interfacial area for use in liquid extraction or chemical reaction between liquids). Drop size of dispersed phase, if initially very fine at high concentrations, increases as the distance downstream increases, owing to coalescence [see Holland, loc. cit.; Ward and Knudsen, *Am. Inst. Chem. Eng. J.,* **13,** 356 (1967)]; or if initially large, decreases by breakup in regions of high shear [Sleicher, ibid., **8,** 471 (1962); *Chem. Eng. Sci.,* **20,** 57 (1965)]. The maximum drop size is given by (Sleicher, loc. cit.)

* Isobutanol dispersed: L_D = 3500 to 27,000; water continuous; L_C = 6000 to 32,000 in pounds-mass per hour-square foot (to convert to kilograms per second-square meter, multiply by 1.36×10^{-3}).

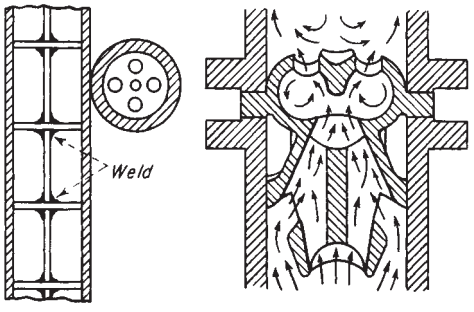


FIG. 18-31 Orifice mixer and nozzle mixer.

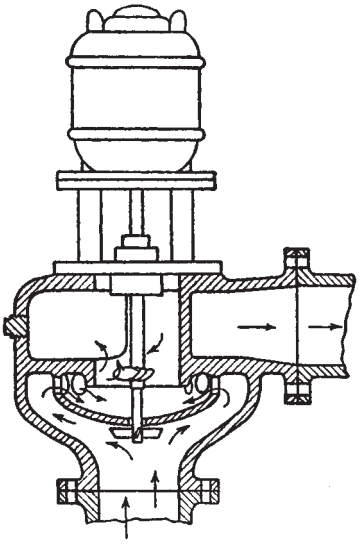


FIG. 18-32 Nettco Corp. Flomix.

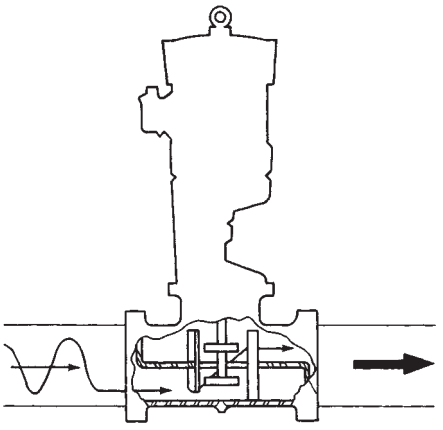


FIG. 18-33 Lightnin line blender. (*Mixing Equipment Co., Inc., with permission.*)

$$\frac{d_{p,\max}\rho_C V^2}{\sigma g_c}\sqrt{\frac{\mu_C V}{\sigma g_c}} = C\left[1 + 0.7\left(\frac{\mu_D V}{\sigma g_c}\right)^{0.7}\right] \qquad (18\text{-}11)$$

where C = 43 (d_t = 0.013 m or 0.0417 ft) or 38 (d_t = 0.038 m or 0.125 ft), with $d_{p,\text{av}} = d_{p,\max}/4$ for high flow rates and $d_{p,\max}/13$ for low velocities.

Extensive measurements of the rate of mass transfer between *n*-butanol and water flowing in a 0.008-m (0.314-in) ID horizontal pipe are reported by Watkinson and Cavers [*Can. J. Chem. Eng.,* **45,** 258 (1967)] in a series of graphs not readily reproduced here. Length of a transfer unit for either phase is strongly dependent upon flow rate and passes through a pronounced maximum at an organic-water phase ratio of 0.5. In energy (pressure-drop) requirements and volume, the pipe line compared favorably with other types of extractors. Boyadzhiev and Elenkov [*Chem. Eng. Sci.,* **21,** 955 (1966)] concluded that, for the extraction of iodine between carbon tetrachloride and water in turbulent flow, drop coalescence and breakup did not influence the extraction rate. Yoshida et al. [*Coal Tar* (Japan), **8,** 107 (1956)] provide details of the treatment of crude benzene with sulfuric acid in a 1-in diameter pipe, N_{Re} = 37,000 to 50,000. Fernandes and Sharma [*Chem. Eng. Sci.,* **23,** 9 (1968)] used cocurrent flow downward of two liquids in a pipe, agitated with an upward current of air.

The pipe has also been used for the transfer of heat between two immiscible liquids in cocurrent flow. For hydrocarbon oil-water, the heat-transfer coefficient is given by

$$\frac{Ua_{\text{av}}d_t^2}{vk_{to}} = \frac{\gamma_D N_{\text{We},t}^{6/5}}{\dfrac{k_{to}}{0.415k_{tC}} + \dfrac{k_{to}}{0.173k_{tD}}} \qquad (18\text{-}12)$$

for γ_D = 0 to 0.2. Additional data for γ_D = 0.4 to 0.8 are also given. Data for stratified flow are given by Wilke et al. [*Chem. Eng. Prog.,* **59,** 69 (1963)] and Grover and Knudsen [*Chem. Eng. Prog.,* **51,** *Symp. Ser.* **17,** 71 (1955)].

Mixing in Agitated Vessels Agitated vessels may frequently be used for either batch or continuous service and for the latter may be sized to provide any holding time desired. They are useful for liquids of any viscosity up to 750 Pa·s (750,000 cP), although in contacting two liquids for reaction or extraction purposes viscosities in excess of 0.1 Pa·s (100 cP) are only rarely encountered.

Mechanical Agitation This type of agitation utilizes a rotating impeller immersed in the liquid to accomplish the mixing and dispersion. There are literally hundreds of devices using this principle, the major variations being found when chemical reactions are being carried out. The basic requirements regarding shape and arrangement of the vessel, type and arrangement of the impeller, and the like are essentially the same as those for dispersing finely divided solids in liquids, which are fully discussed in Sec. 18.

The following summary of operating characteristics of mechanically agitated vessels is confined to the data available on liquid-liquid contacting.

Phase Dispersed There is an ill-defined upper limit to the volume fraction of dispersed liquid which may be maintained in an agitated dispersion. For dispersions of organic liquids in water [Quinn and Sigloh, *Can. J. Chem. Eng.,* **41,** 15 (1963)],

$$\gamma_{Do,\max} = \gamma' + \left(\frac{C}{N^3}\right) \qquad (18\text{-}13)$$

where γ' is a constant, asymptotic value, and C is a constant, both depending in an unestablished manner upon the system physical properties and geometry. Thus, inversion of a dispersion may occur if the agitator speed is increased. With systems of low interfacial tension (σ' = 2 to 3 mN/m or 2 to 3 dyn/cm), γ_D as high as 0.8 can be maintained. Selker and Sleicher [*Can. J. Chem. Eng.,* **43,** 298 (1965)] and Yeh et al. [*Am. Inst. Chem. Eng. J.,* **10,** 260 (1964)] feel that the viscosity ratio of the liquids alone is important. Within the limits in which either phase can be dispersed, for *batch operation* of baffled vessels, that phase in which the impeller is immersed when at rest will normally be continuous [Rodger, Trice, and Rushton, *Chem. Eng. Prog.,* **52,** 515 (1956); Laity and Treybal, *Am. Inst. Chem. Eng. J.,* **3,** 176 (1957)]. With water dispersed, *dual emulsions* (continuous phase found as small droplets within larger drops of dispersed phase) are possible. In *continuous operation,* the vessel is first filled with the liquid to be continuous, and agitation is then begun, after which the liquid to be dispersed is introduced.

Uniformity of Mixing This refers to the gross uniformity throughout the vessel and not to the size of the droplets produced. For *unbaffled vessels, batch, with an air-liquid interface,* Miller and Mann [*Trans. Am. Inst. Chem. Eng.,* **40,** 709 (1944)] mixed water with several organic liquids, measuring uniformity of mixing by sampling the tank at various places, comparing the percentage of dispersed phase found with that in the tank as a whole. A power application of 200 to 400 W/m^3 [(250 to 500 ft·lb)/(min·ft^3)] gave maximum and nearly uniform performance for all. See also Nagata et al. [*Chem. Eng. (Japan),* **15,** 59 (1951)].

For *baffled vessels operated continuously, no air-liquid interface,* flow upward, light liquid dispersed [Treybal, *Am. Inst. Chem. Eng. J.,* **4,** 202 (1958)], the average fraction of dispersed phase in the vessel $\gamma_{D,\text{av}}$ is less than the fraction of the dispersed liquid in the feed mixture, unless the impeller speed is above a certain critical value which depends upon vessel geometry and liquid properties. Thornton and Bouyatiotis [*Ind. Chem.,* **39,** 298 (1963); *Inst. Chem. Eng. Symp. Liquid Extraction,* Newcastle-upon-Tyne, April 1967] have presented correlations of data for a 17.8-cm (7-in) vessel, but these do not agree with observations on 15.2- and 30.5-cm (6- and 12-in) vessels in Treybal's laboratory. See also Kovalev and Kagan [*Zh. Prikl. Khim.,* **39,** 1513 (1966)] and Trambouze [*Chem. Eng. Sci.,* **14,** 161 (1961)]. Stemerding et al. [*Can. J. Chem. Eng.,* **43,** 153 (1965)] present data on a large mixing tank [15 m^3 (530 ft^3)] fitted with a marine-type propeller and a draft tube.

Drop Size and Interfacial Area The drops produced have a size range [Sullivan and Lindsey, *Ind. Eng. Chem. Fundam.,* **1,** 87 (1962); Sprow, *Chem. Eng. Sci.,* **22,** 435 (1967); and Chen and Middleman, *Am. Inst. Chem. Eng. J.,* **13,** 989 (1967)]. The average drop size may be expressed as

$$d_{p,\text{av}} = \frac{\sum n_i d_{pi}^3}{\sum n_i d_{pi}^2} \qquad (18\text{-}14)$$

and if the drops are spherical,

$$a_{\text{av}} = \frac{6\gamma_{D,\text{av}}}{d_{p,\text{av}}} \qquad (18\text{-}15)$$

The drop size varies locally with location in the vessel, being smallest at the impeller and largest in regions farthest removed from the impeller owing to coalescence in regions of relatively low turbulence

intensity [Schindler and Treybal, *Am. Inst. Chem. Eng. J.,* **14,** 790 (1968); Vanderveen, U.S. AEC UCRL-8733, 1960]. Interfacial area and hence average drop size have been measured by light transmittance, light scattering, direct photography, and other means. Typical of the resulting correlations is that of Thornton and Bouyatiotis (*Inst. Chem. Eng. Symp. Liquid Extraction,* Newcastle-upon-Tyne, April 1967) for a 17.8-cm- (7-in-) diameter baffled vessel, six-bladed flat-blade turbine, $d_i = 6.85$ cm (0.225 ft), operated full, for organic liquids ($\sigma' = 8.5$ to 34, $\rho_D = 43.1$ to 56.4, $\mu_D = 1.18$ to 1.81) dispersed in water, in the absence of mass transfer, and under conditions giving nearly the vessel-average $d_{p,av}$:

$$\frac{d_{p,av}}{d_p^0} = 1 + 1.18\phi_D \left(\frac{\sigma^2 g_c^2}{d_p^0 \mu_c^2 g}\right)\left(\frac{\mu_c^4 g}{\Delta\rho\, \sigma^3 g_c^3}\right)^{0.62}\left(\frac{\Delta\rho}{\rho_c}\right)^{0.05} \quad (18\text{-}16)$$

where d_p^0 is given by

$$\frac{(d_p^0)^3 \rho_C^2 g}{\mu_c^2} = 29.0\left(\frac{P^3 g_c^3}{v^3 \rho_c^2 \mu_c g^4}\right)^{-0.32}\left(\frac{\rho_C \sigma^3 g_c^3}{\mu_c^4 g}\right)^{0.14} \quad (18\text{-}17)$$

Caution is needed in using such correlations, since those available do not generally agree with each other. For example, Eq. (21-28) gives $d_{p,av} = 4.78(10^{-4})$ ft for a liquid pair of properties $a' = 30$, $\rho_C = 62.0$, $\rho_D = 52.0$, $\mu_C = 2.42$, $\mu_D = 1.94$, $\gamma_{D,av} = 0.20$ in a vessel $T = Z = 0.75$, a turbine impeller $d_i = 0.25$ turning at 400 r/min. Other correlations provide $3.28(10^{-4})$ [Thornton and Bouyatiotis, *Ind. Chem.,* **39,** 298 (1963)], $8.58(10^{-4})$ [Calderbank, *Trans. Inst. Chem. Eng. (London),* **36,** 443 (1958)], $6.1(10^{-4})$ [Kafarov and Babinov, *Zh. Prikl. Khim,* **32,** 789 (1959)], and $2.68(10^{-3})$ (Rushton and Love, paper at AIChE, Mexico City, September 1967). See also Vermeulen et al. [*Chem. Eng. Prog.,* **51,** 85F (1955)], Rodgers et al. [ibid., **52,** 515 (1956); U.S. AEC ANL-5575 (1956)], Rodrigues et al. [*Am. Inst. Chem. Eng. J.,* **7,** 663 (1961)], Sharma et al. [*Chem. Eng. Sci.,* **21,** 707 (1966); **22,** 1267 (1967)], and Kagan and Kovalev [*Khim. Prom.,* **42,** 192 (1966)]. For the effect of absence of baffles, see Fick et al. (U.S. AEC UCRL-2545, 1954) and Schindler and Treybal [*Am. Inst. Chem. Eng. J.,* **14,** 790 (1968)]. The latter have observations during mass transfer.

Coalescence Rates The droplets coalesce and redisperse at rates that depend upon the vessel geometry, N, $\gamma_{D,av}$, and liquid properties. The few measurements available, made with a variety of techniques, do not as yet permit quantitative estimates of the coalescence frequency v. Madden and Damarell [*Am. Inst. Chem. Eng. J.,* **8,** 233 (1962)] found for baffled vessels that v varied as $N^{2.2}\gamma_{D,av}^{0.5}$, and this has generally been confirmed by Groothius and Zuiderweg [*Chem. Eng. Sci.,* **19,** 63 (1964)], Miller et al. [*Am. Inst. Chem. Eng. J.,* **9,** 196 (1963)], and Howarth [ibid., **13,** 1007 (1967)], although absolute values of v in the various studies are not well related. Hillestad and Rushton (paper at AIChE, Columbus, Ohio, May 1966), on the other hand, find v to vary as $N^{0.73}\gamma_{D,av}$ for impeller Weber numbers $N_{We,i}$ below a certain critical value and as $N^{-3.5}\gamma_{D,av}^{1.58}$ for higher Weber numbers. The influence of liquid properties is strong. There is clear evidence [Groothius and Zuiderweg, loc. cit.; *Chem. Eng. Sci.,* **12,** 288 (1960)] that coalescence rates are enhanced by mass transfer from a drop to the surrounding continuum and retarded by transfer in the reverse direction. See also Howarth [*Chem. Eng. Sci.,* **19,** 33 (1964)]. For a theoretical treatment of drop breakage and coalescence and their effects, see Valentas and Amundsen [*Ind. Eng. Chem. Fundam.,* **5,** 271, 533 (1966); **7,** 66 (1968)], Gal-Or and Walatka [*Am. Inst. Chem. Eng. J.,* **13,** 650 (1967)], and Curl [ibid., **9,** 175 (1963)].

In calculating the power required for mixers, a reasonable estimate of the average density and viscosity for a two-phase system is satisfactory.

Solids are often present in liquid streams either as a part of the processing system or as impurities that come along and have to be handled in the process. One advantage of mixers in differential contact equipment is the fact that they can handle slurries in one or both phases. In many industrial leaching systems, particularly in the minerals processing industry, coming out of the leach circuit is a slurry with a desired material involved in the liquid but a large amount of solids contained in the stream. Typically, the solids must be separated out by filtration or centrifugation, but there has always been a desire to try a direct liquid-liquid extraction with an immiscible liquid contact with this often highly concentrated slurry leach solution. The major problem with this approach is loss of organic material going out with the highly concentrated liquid slurry.

Data are not currently available on the dispersion with the newer fluidfoil impellers, but they are often used in industrial mixer-settler systems to maintain dispersion when additional resonance time holdup is required, after an initial dispersion is made by a radial- or axial-flow turbine.

Recent data by Calabrese[5] indicates that the sauter mean drop diameter can be correlated by equation and is useful to compare with other predictions indicated previously.

As an aside, when a large liquid droplet is broken up by shear stress, it tends initially to elongate into a dumbbell shape, which determines the particle size of the two large droplets formed. Then, the neck in the center between the ends of the dumbbell may explode or shatter. This would give a debris of particle sizes which can be quite different than the two major particles produced.

Liquid-Liquid Extraction The actual configuration of mixers in multistage mixer-settlers and/or multistage columns is summarized in Section 15. A general handbook on this subject is *Handbook of Solvent Extraction* by Lowe, Beard, and Hanson. This handbook gives a comprehensive review of this entire operation as well.

In the liquid-liquid extraction area, in the mining industry, coming out of the leach tanks is normally a slurry, in which the desired mineral is dissolved in the liquid phase. To save the expense of separation, usually by filtration or centrifugation, attempts have been made to use a resident pump extraction system in which the organic material is contacted directly with the slurry. The main economic disadvantage to this proposed system is the fact that considerable amounts of organic liquid are entrained in the aqueous slurry system, which, after the extraction is complete, is discarded. In many systems this has caused an economic loss of solvent into this waste stream.

LIQUID-LIQUID-SOLID SYSTEMS

Many times solids are present in one or more phases of a solid-liquid system. They add a certain level of complexity in the process, especially if they tend to be a part of both phases, as they normally will do. Approximate methods need to be worked out to estimate the density of the emulsion and determine the overall velocity of the flow pattern so that proper evaluation of the suspension requirements can be made. In general, the solids will behave as though they were a fluid of a particular average density and viscosity and won't care much that there is a two-phase dispersion going on in the system. However, if solids are being dissolved or precipitated by participating in one phase and not the other, then they will be affected by which phase is dispersed or continuous, and the process will behave somewhat differently than if the solids migrate independently between the two phases within the process.

FLUID MOTION

Pumping Some mixing applications can be specified by the pumping capacity desired from the impeller with a certain specified geometry in the vessel. As mentioned earlier, this sometimes is used to describe a blending requirement, but circulation and blending are two different things. The major area where this occurs is in draft tube circulators or pump-mix mixer settlers. In draft tube circulators (shown in Fig. 18-22), the circulation occurs through the draft tube and around the annulus and for a given geometry, the velocity head required can be calculated with reference to various formulas for geometric shapes. What is needed is a curve for head versus flow for the impeller, and then the system curve can be matched to the impeller curve. Adding to the complexity of this system is the fact that solids may settle out and change the character of the head curve so that the impeller can get involved in an unstable condition which has various degrees of erratic behavior depending upon the sophistication of the impeller and inlet and outlet vanes involved. These draft tube circulators often involve solids, and applications are often for precipitation or crystallization in these units. Draft tube circulators

can either have the impeller pump up in the draft tube and flow down the annulus or just the reverse. If the flow is down the annulus, then the flow has to make a 180° turn where it comes back at the bottom of the tank into the draft tube again. This is a very sensitive area, and special baffles must be used to carefully determine how the fluid will make this turn since many areas of constriction are involved in making this change in direction.

When pumping down the draft tube, flow normally makes a more troublefree velocity change to a flow going up the annulus. Since the area of the draft tube is markedly less than the area of the annulus, pumping up the draft tube requires less flow to suspend solids of a given settling velocity than does pumping down the draft tube.

Another example is to eliminate the interstage pump between mixing and settling stages in the countercurrent mixer-settler system. The radial-flow impeller typically used is placed very close to an orifice at the bottom of the mixing tank and can develop heads from 12 to 18 in. All the head-loss terms in the mixer and settler circuit have to be carefully calculated because they come very close to that 12- to 18-in range when the passages are very carefully designed and streamlined. If the mixing tank gets much above 10 ft in depth, then the heads have to be higher than the 12- to 18-in range and special designs have to be worked on which have the potential liability of increasing the shear rate acting on the dispersed phase to cause more entrainment and longer settling times. In these cases, it is sometimes desirable to put the mixer system outside the actual mixer tank and have it operate in a single phase or to use multiple impellers, each one of which can develop a portion of the total head required.

Heat Transfer In general, the fluid mechanics of the film on the mixer side of the heat transfer surface is a function of what happens at that surface rather than the fluid mechanics going on around the impeller zone. The impeller largely provides flow across and adjacent to the heat-transfer surface and that is the major consideration of the heat-transfer result obtained. Many of the correlations are in terms of traditional dimensionless groups in heat transfer, while the impeller performance is often expressed as the impeller Reynolds number.

The fluidfoil impellers (shown in Fig. 18-2) usually give more flow for a given power level than the traditional axial- or radial-flow turbines. This is also thought to be an advantage since the heat-transfer surface itself generates the turbulence to provide the film coefficient and more flow should be helpful. This is true to a limited degree in jacketed tanks (Fig. 18-34), but in helical coils (Fig. 18-35), the extreme axial flow of these impellers tends to have the first or second turn in the coil at the bottom of the tank blank off the flow from the turns above it in a way that (at the same power level) the increased flow from the fluidfoil impeller is not helpful. It best gives the same coefficient as with the other impellers and on occasion can cause a 5 to 10 percent reduction in the heat-transfer coefficient over the entire coil.

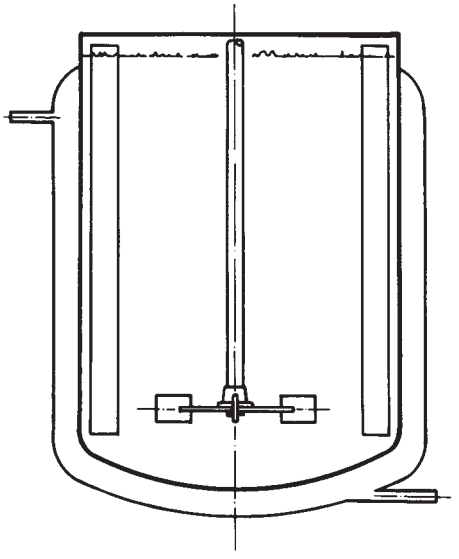


FIG. 18-34 Typical jacket arrangement for heat transfer.

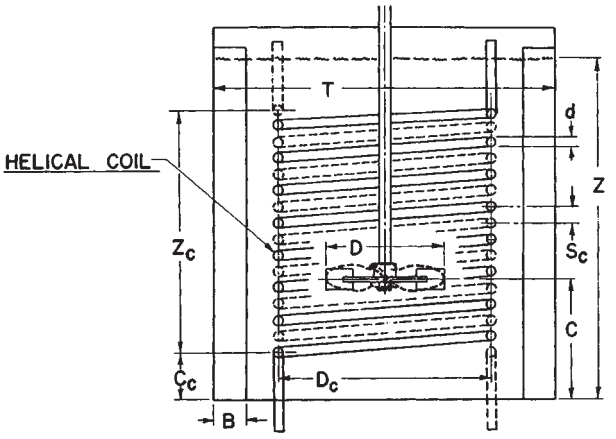


FIG. 18-35 Typical arrangement of helical coil at mixing vessel for heat transfer.

JACKETS AND COILS OF AGITATED VESSELS

Most of the correlations for heat transfer from the agitated liquid contents of vessels to jacketed walls have been of the form:

$$\frac{hD_j}{k} = a\left(\frac{L_p^2 N_r \rho}{\mu}\right)^b \left(\frac{c\mu}{k}\right)^{1/3} \left(\frac{\mu_b}{\mu_w}\right)^m \qquad (18\text{-}18)$$

The film coefficient h is for the inner wall; D_j is the inside diameter of the mixing vessel. The term $L_p^2 N_r \rho/\mu$ is the Reynolds number for mixing in which L_p is the diameter and N_r the speed of the agitator. Recommended values of the constants a, b, and m are given in Table 18-2.

A wide variety of configurations exists for coils in agitated vessels. Correlations of data for heat transfer to helical coils have been of two forms, of which the following are representative:

$$\frac{hD_j}{k} = 0.87\left(\frac{L_p^2 N_t \rho}{\mu}\right)^{0.62} \left(\frac{c\mu}{k}\right)^{1/3} \left(\frac{\mu_b}{\mu_w}\right)^{0.14} \qquad (18\text{-}19)$$

TABLE 18-2 Values of Constants for Use in Eq. (18-18)

Agitator	a	b	m	Range of Reynolds number
Paddle[a]	0.36	⅔	0.21	$300–3 \times 10^5$
Pitched-blade turbine[b]	0.53	⅔	0.24	80–200
Disk, flat-blade turbine[c]	0.54	⅔	0.14	$40–3 \times 10^5$
Propeller[d]	0.54	⅔	0.14	2×10^3 (one point)
Anchor[b]	1.0	½	0.18	10–300
Anchor[b]	0.36	⅔	0.18	300–40,000
Helical ribbon[e]	0.633	½	0.18	$8–10^5$

[a]Chilton, Drew, and Jebens, *Ind. Eng. Chem.*, **36,** 510 (1944), with constant m modified by Uhl.
[b]Uhl, *Chem. Eng. Progr., Symp. Ser.* 17, **51,** 93 (1955).
[c]Brooks and Su, *Chem. Eng. Progr.*, **55**(10), 54 (1959).
[d]Brown et al., *Trans. Inst. Chem. Engrs.* (*London*), **25,** 181 (1947).
[e]Gluz and Pavlushenko, *J. Appl. Chem. U.S.S.R.*, **39,** 2323 (1966).

where the agitator is a paddle, the Reynolds number range is 300 to 4×10^5 [Chilton, Drew, and Jebens, *Ind. Eng. Chem.*, **36,** 510 (1944)], and

$$\frac{hD_o}{k} = 0.17\left(\frac{L_p^2 N_r \rho}{\mu}\right)^{0.67}\left(\frac{c\mu}{k}\right)^{0.37}\left(\frac{L_p}{D_j}\right)^{0.1}\left(\frac{D_o}{D_j}\right)^{0.5} \qquad (18\text{-}20)$$

where the agitator is a disk flat-blade turbine, and the Reynolds number range is 400 to $(2)(10^5)$ [Oldshue and Gretton, *Chem. Eng. Prog.*, **50,** 615 (1954)]. The term D_o is the outside diameter of the coil tube.

The most comprehensive correlation for heat transfer to vertical baffle-type coils is for a disk flat-blade turbine over the Reynolds number range 10^3 to $(2)(10^6)$:

$$\frac{hD_o}{k} = 0.09\left(\frac{L_p^2 N_r \rho}{\mu}\right)^{0.65}\left(\frac{c\mu}{k}\right)^{1/3}\left(\frac{L_p}{D_j}\right)^{1/3}\left(\frac{2}{n_b}\right)^{0.2}\left(\frac{\mu}{\mu_f}\right)^{0.4} \qquad (18\text{-}21)$$

where n_b is the number of baffle-type coils and μ_f is the fluid viscosity at the mean film temperature [Dunlop and Rushton, *Chem. Eng. Prog. Symp. Ser.* 5, **49,** 137 (1953)].

Chapman and Holland (*Liquid Mixing and Processing in Stirred Tanks,* Reinhold, New York, 1966) review heat transfer to low-viscosity fluids in agitated vessels. Uhl ["Mechanically Aided Heat Transfer," in Uhl and Gray (eds.), *Mixing: Theory and Practice,* vol. I, Academic, New York, 1966, chap. V] surveys heat transfer to low- and high-viscosity agitated fluid systems. This review includes scraped-wall units and heat transfer on the jacket and coil side for agitated vessels.

LIQUID-LIQUID-GAS-SOLID SYSTEMS

This is a relatively unusual combination, and one of the more common times it exists is in the fermentation of hydrocarbons with aerobic microorganisms in an aqueous phase. The solid phase is a microorganism which is normally in the aqueous phase and is using the organic phase for food. Gas is supplied to the system to make the fermentation aerobic. Usually the viscosities are quite low, percent solids is also modest, and there are no special design conditions required when this particular gas-liquid-liquid-solid combination occurs. Normally, average properties for the density of viscosity of the liquid phase are used. In considering that the role the solids play in the system is adequate, there are cases of other processes which consist of four phases, each of which involves looking at the particular properties of the phases to see whether there are any problems of dispersion, suspension, or emulsification.

COMPUTATIONAL FLUID DYNAMICS

There are several software programs that are available to model flow patterns of mixing tanks. They allow the prediction of flow patterns based on certain boundary conditions. The most reliable models use accurate fluid mechanics data generated for the impellers in question and a reasonable number of modeling cells to give the overall tank flow pattern. These flow patterns can give velocities, streamlines, and localized kinetic energy values for the systems. Their main use at the present time is to look at the effect of making changes in mixing variables based on doing certain things to the mixing process. These programs can model velocity, shear rates, and kinetic energy, but probably cannot adapt to the actual chemistry of diffusion or mass-transfer kinetics of actual industrial process at the present time.

Relatively uncomplicated transparent tank studies with tracer fluids or particles can give a similar feel for the overall flow pattern. It is important that a careful balance be made between the time and expense of calculating these flow patterns with computational fluid dynamics compared to their applicability to an actual industrial process. The future of computational fluid dynamics appears very encouraging and a reasonable amount of time and effort put forth in this regard can yield immediate results as well as potential for future process evaluation.

Figures 18-36, 18-37, and 18-38 show some approaches. Figure 18-36 shows velocity vectors for an A310 impeller. Figure 18-37 shows contours of kinetic energy of turbulence. Figure 18-38 uses a particle trajectory approach with neutral buoyancy particles.

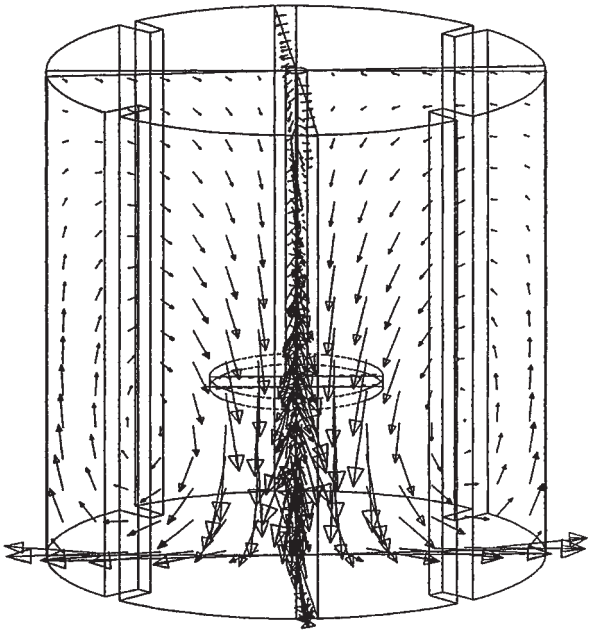


FIG. 18-36 Laser scan.

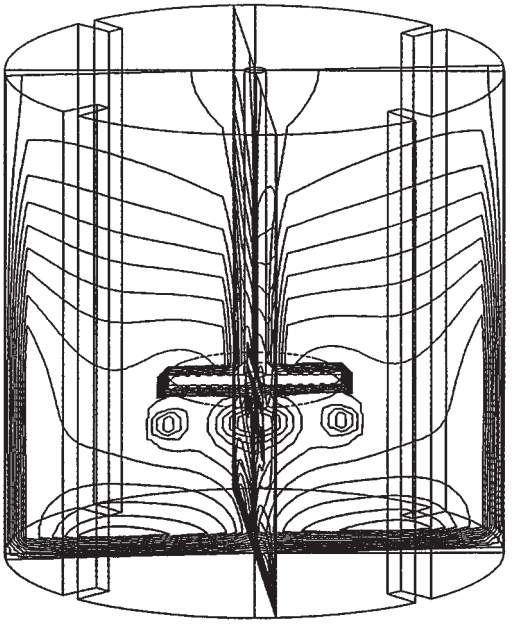


FIG. 18-37 Laser scan.

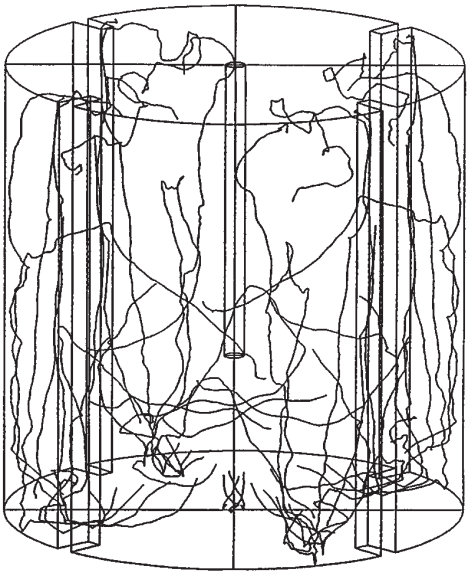


FIG. 18-38 Laser scan.

Numerical fluid mechanics can define many of the fluid mechanics parameters for an overall reactor system. Many of the models break up the mixing tank into small microcells. Suitable material and mass-transfer balances between these cells throughout the reactor are then made. This can involve long and massive computational requirements. Programs are available that can give reasonably acceptable models of experimental data taken in mixing vessels. Modeling the three-dimensional aspect of a flow pattern in a mixing tank can require a large amount of computing power.

Most modeling codes are a time-averaging technique. Depending upon the process, a time-dependent technique may be more suitable. Time-dependent modeling requires much more computing power than does time averaging.

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PASTE AND VISCOUS-MATERIAL MIXING

GENERAL REFERENCES: *Dry Solids, Paste and Dough Mixing Equipment Testing Procedure,* American Institute of Chemical Engineers, New York, 1979. Fischer, *Chem. Eng.* **69**(3): 52 (1962). Irving and Saxton, "Mixing of High Viscosity Materials," in Uhl and Gray, *Mixing Theory and Practice,* vol. 2, Academic, New York, 1967, chap. 8. Mohr, in Bernhardt, *Processing of Thermoplastic Materials,* Reinhold, New York, 1967, chap. 3. Parker, *Chem. Eng.* **71**(12): 166 (1964). Rauwendaal, *Mixing in Polymer Processing,* Marcel Dekker, 1991. Tadmor and Gogos, *Principles of Polymer Processing,* Wiley, New York, 1979.

INTRODUCTION

Thick mixtures with viscosities greater than 10 Pa·s are not readily mixed in conventional stirred pots with either propeller or turbine agitators. The high viscosity may be due to that of the matrix fluid itself, to a high slurry concentration, or to interactions between components.

Because of the high viscosity, the mixing Reynolds number ($Re = D^2\rho N/\mu$) may be well below 100. Mixing occurs as a consequence of laminar shearing and stretching forces, and turbulence plays no part. Relative motion of an agitator stretches and deforms the material between itself and the vessel wall. As a layer of fluid gets stretched into thinner layers, the striations diminish and the shear forces tear solid agglomerates apart until apparent homogeneity is obtained. When solids are present, it may be necessary to reduce the particle size of the solids, even down to submicron size, such as in pigment dispersion.

Mixers for high-viscosity materials generally have a small high shear zone (to minimize dissipative heat effects) and rely on the impeller to circulate all of the mixer contents past the high shear zone. It may be necessary to take special steps to eliminate any stagnant zones or perhaps to avoid material riding around on mixing blades without being reincorporated into the matrix.

Most paste and high-viscosity mixtures are nonnewtonian, with viscosity dropping with shear rate. Consequently, increasing impeller speed may be counterproductive, as the transmitted shear drops rapidly and an isolated hole may be created in the central mass without circulation of the bulk material in the remainder of the vessel.

The relative viscosities of the materials being mixed can be very important. Karam and Bellinger [*Ind. Eng. Chem. Fund.* **7:** 576 (1981)] and Grace [*Engr. Fndn. Mixing Research Conf.* Andover, N.H., 1973] have shown that there is a maximum viscosity ratio (μ dispersed/μ continuous equal to about 4) above which droplets can no longer be dispersed by shear forces. The only effective dispersing mechanism for high-viscosity-ratio mixtures is elongational flow.

Equipment for viscous mixing usually has a small clearance between impeller and vessel walls, a relatively small volume, and a high power per unit volume. Intermeshing blades or stators may be present to prevent material from cylindering on the rotating impeller.

Blade shape can have a significant impact on the mixing process. A scraping profile will be useful if heat transfer is important, whereas a smearing profile will be more effective for dispersion. Ease of cleaning and ease of discharge may also be important.

BATCH MIXERS

Change-Can Mixers Change-can mixers are vertical batch mixers in which the container is a separate unit easily placed in or removed from the frame of the machine. They are available in capacities of about 4 to 1500 L (1 to 400 gal). The commonest type is the pony mixer. Separate cans allow the batch to be carefully measured or weighed before being brought to the mixer itself. The mixer also may serve to transport the finished batch to the next operation or to storage. The identity of each batch is preserved, and weight checks are easily made.

Change cans are relatively inexpensive. A good supply of cans allows cleaning to be done in a separate department, arranged for efficient cleaning. In paint and ink plants, where mixing precedes milling or grinding and where there may be a long run of the same formulation and color, the cans may be used for an extended period without cleaning, as long as no drying out or surface oxidation occurs.

In most change-can mixers, the mixing elements are raised from the can by either a vertical lift or a tilting head; in others, the can is

dropped away from the mixing elements. After separation the mixing elements drain into the can, and the blades can be wiped down. With the can out of the way, complete cleaning in the blades and their supports is simple. If necessary, blades may be cleaned by rotating them in solvent.

Intimate mixing is accomplished in change-can mixers in two ways. One method is to have the mixing-unit assembly revolve in a planetary motion so that the rotating blades sweep the entire circumference of the can (Fig. 18-39). The other is to mount the can on a rotating turntable so that all parts of the can wall pass fixed scraper blades or the agitator blades at a point of minimum clearance.

A type of heavy-duty planetary change-can mixer has been used extensively for processing critical solid-propellant materials. In a design offered by APV Chemical Machinery Inc., the mixer blades pass through all portions of the can volume, and the two blades wipe each other, thus assuring no unmixed portions. A dead spot under the mixer blades is avoided by having both blades off the centerline of the can. The cans fit tightly enough so that mixing can be achieved under vacuum or pressure. There is no contact between the glands and the material being mixed. Charging ports located in the housing directly above the mixing can make it possible to charge materials to the mixer with the can in the operating position. This type of mixer is available in sizes of 0.5 L (about 1 pt) to 1.6 m^3 (420 gal), involving power input of 0.2 to 75 kW (0.25 to 100 hp).

Helical-Blade Mixers Helical mixers are now available in a variety of configurations. The mixing element may be in the form of a conical or a cylindrical helix. It may be a ribbon spaced radially from the shaft by spokes or a screw consisting of a helical surface that is continuous from the shaft to the periphery of the helix. A venerable example of the latter type is the soap crutcher, in which the screw is mounted in a draft tube. Close screw-tube clearance and a high rotational speed result in rapid motion of the material and high shear. The screw lifts the material through the tube, and gravity returns it to the bottom of the tank. If the tank has well-rounded corners, this kind of mixer may be used for fibrous materials. Heavy paper pulp containing 16 to 18 percent solids is uniformly bleached in large mixers of this type.

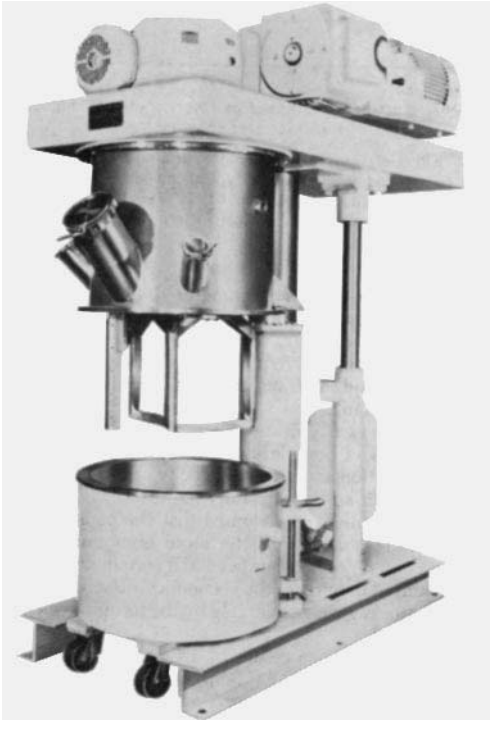


FIG. 18-39 Change-can mixer. (*Charles Ross & Son Co.*)

A double helix shortens mixing time but requires more power. The disadvantages of the higher torque requirement are frequently offset by the better mixing and heat transfer.

A vertical helical ribbon blender can be combined with an axial screw of smaller diameter (Fig. 18-25). Such mixers are used in polymerization reactions in which uniform blending is required but in which high-shear dispersion is not a factor. Addition of the inner flight contributes little more turnover in mixing newtonian fluids but significantly shortens the mixing time in nonnewtonian systems and adds negligibly to the impeller power [Coyle et al., *Am. Inst. Chem. Eng. J.*, **15,** 903 (1970)].

Double-Arm Kneading Mixers The universal mixing and kneading machine consists of two counterrotating blades in a rectangular trough curved at the bottom to form two longitudinal half cylinders and a saddle section (Fig. 18-40). The blades are driven by gearing at either or both ends. The oldest style empties through a bottom door or valve and is still in use when 100 percent discharge or thorough cleaning between batches is not an essential requirement. More commonly, however, double-arm mixers are tilted for discharge. The tilting mechanism may be manual, mechanical, or hydraulic.

A variety of blade shapes has evolved. The mixing action is a combination of bulk movement, smearing, stretching, folding, dividing, and recombining as the material is pulled and squeezed against blades, saddle, and sidewalls. The blades are pitched to achieve end-to-end circulation. Rotation is usually such that material is drawn down over the saddle. Clearances are as close as 1 mm (0.04 in).

The blades may be tangential or overlapping. Tangential blades are run at different speeds, with the advantages of faster mixing from constant change of relative position, greater wiped heat-transfer area per unit volume, and less riding of material above the blades. Overlapping blades can be designed to avoid buildup of sticky material on the blades.

The agitator design most widely used is the sigma blade (Fig. 18-41*a*). The sigma-blade mixer is capable of starting and operating with either liquids or solids or a combination of both. Modifications in blade-face design have been introduced to increase particular effects, such as shredding or wiping. The sigma blade has good mixing action, readily discharges materials which do not stick to the blades, and is relatively easy to clean when sticky materials are being processed.

The dispersion blade (Fig. 18-41*b*) was developed particularly to provide compressive shear higher than that achieved with standard

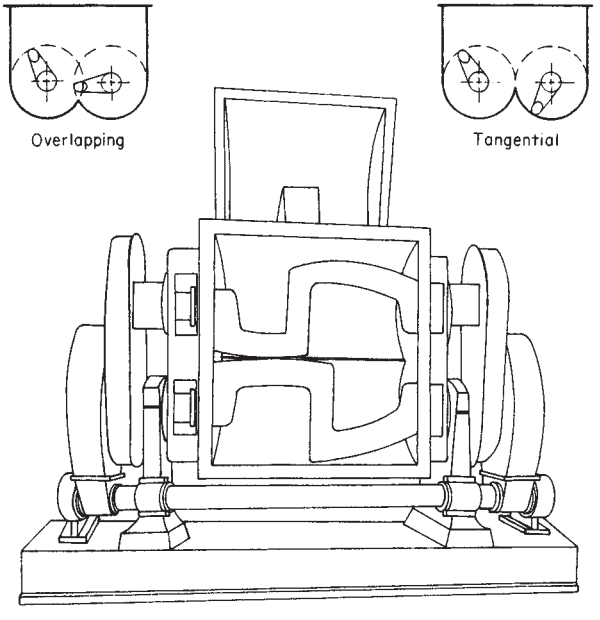


FIG. 18-40 Double-arm kneader mixer. (*APV Baker Perkins Inc.*)

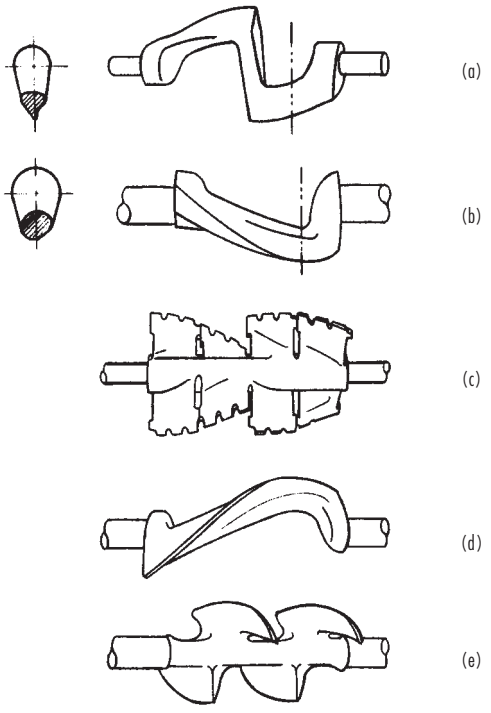


FIG. 18-41 Agitator blades for double-arm kneaders: (*a*) sigma; (*b*) dispersion; (*c*) multiwiping overlap; (*d*) single-curve; (*e*) double-naben. (*APV Baker Perkins, Inc.*)

sigma blades. The blade face wedges material between itself and the trough, rather than scraping the trough, and is particularly suited for dispersing fine particles in a viscous mass. Rubbery materials have a tendency to ride the blades, and a ram is frequently used to keep the material in the mixing zone.

Multiwiping overlapping (MWOL) blades (Fig. 18-41*c*) are commonly used for mixtures which start tough and rubberlike, inasmuch as the blade cuts the material into small pieces before plasticating it.

The single-curve blade (Fig. 18-41*d*) was developed for incorporating fiber reinforcement into plastics. In this application, the individual fibers (e.g., sisal or glass) must be wetted with polymer without incurring undue fiber breakage.

Many other blade designs have been developed for specific applications. The double-naben blade (Fig. 18-41*e*) is a good blade for mixes which "ride," that is, form a lump which bridges across the sigma blade.

Double-arm mixers are available from several suppliers (e.g., Paul O. Abbe, Inc.; Littleford Day; Jaygo, Inc.; Charles Ross & Son Co.; Teledyne Readco). Options include vacuum design, cored blades, jacketed trough, choice of cover design, and a variety of seals and packing glands. Power requirements vary from ⅛ to 2 hp/gal of capacity. Table 18-3 lists specifications and space requirements for typical tilting-type, double-ended-drive, double-arm mixers. The working capacity is generally at or near the top of the blades, and the total capacity is the volume contained when the mixer is filled level with the top of the trough.

Figure 18-42 provides a guide for typical applications. Individual formulation changes may require more power than indicated in the figure. Parker [*Chem. Eng.*, **72**(18), 121 (1965)] has described in greater detail how to select double-arm mixers.

Screw-Discharge Batch Mixers A variant of the sigma-blade mixer is now available with an extrusion-discharge screw located in the saddle section. During the mixing cycle the screw moves the material within the reach of the mixing blades, thereby accelerating the mixing process. At discharge time, the direction of rotation of the screw is reversed and the mixed material is extruded through suitable die openings in the side of the machine. The discharge screw is driven independently of the mixer blades by a separate drive.

Working capacities range from 4 to 3800 L (1 to 1000 gal), with up to 300 kW (400 hp). This type of kneader is offered by most of the double-arm-kneader manufacturers. It is particularly suitable when a heel from the prior batch can be left without detriment to succeeding batches.

TABLE 18-3 Characteristics of Double-Arm Kneading Mixers*

Size number	Capacity, U.S. gal		Typical supplied horsepower		Floor space, ft
	Working	Maximum	Sigma blade, MWOL blade	Dispersion blade	
4	0.7	1	1	2	1 × 3
6	2.3	3.5	2	5	2 × 3
8	4.5	7	5	7.5	3 × 4
11	10	15	15	20	5 × 6
12	20	30	25	40	6 × 6
14	50	75	30	60	6 × 8
15	100	150	50	100	8 × 10
16	150	225	60	150	9 × 11
17	200	300	75	200	9 × 13
18	300	450	100	—	10 × 14
20	500	750	150	—	11 × 16
21	600	900	175	—	12 × 16
22	750	1125	225	—	12 × 17
23	1000	1500	300	—	14 × 18

*Data from APV Baker Perkins, Inc. To convert feet to meters, multiply by 0.3048; to convert gallons to cubic meters, multiply by 3.78×10^{-3}; and to convert horsepower to kilowatts, multiply by 0.746.

Intensive Mixers

Banbury Mixer Preeminent in the field of high-intensity mixers, with power input up to 6000 kW/m^3 (30 hp/gal), is the Banbury mixer, made by the Farrel Co. (Fig. 18-43). It is used mainly in the plastics and rubber industries. The top of the charge is confined by an air-operated ram cover mounted so that it can be forced down on the charge. The clearance between the rotors and the walls is extremely small, and it is

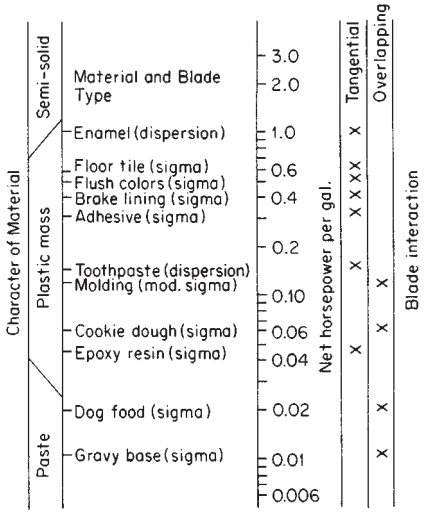


FIG. 18-42 Typical application and power for double-arm kneaders. To convert horsepower per gallon to kilowatts per cubic meter, multiply by 197.3. [*Parker,* Chem. Eng. **72***(18): 125 (1965); excerpted by special permission of the copyright owner, McGraw-Hill, Inc.*]

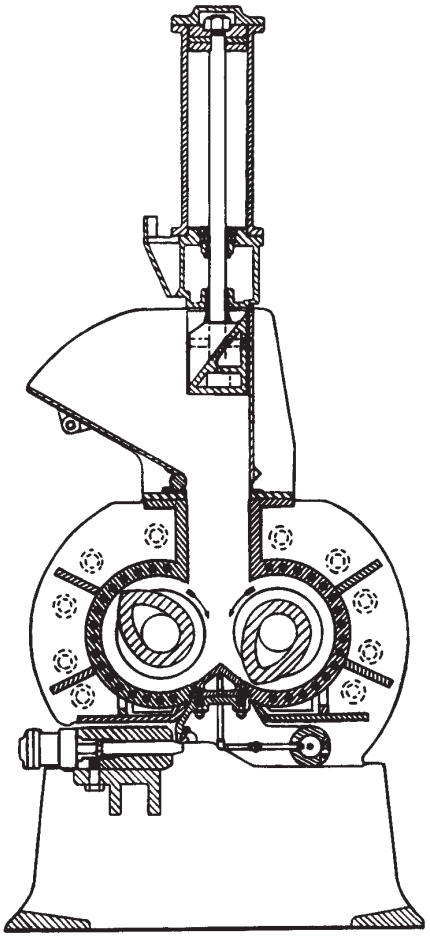


FIG. 18-43 Banbury mixer. (*Farrel Co.*)

here that the mixing action takes place. The operation of the rotors of a Banbury at different speeds enables one rotor to drag the stock against the rear of the other and thus help clean ingredients from this area.

The extremely high power consumption of the machines operating at speeds of 40 r/min or lower calls for rotor shafts of large diameter. The combination of heavy shafts, stubby blades, close clearances, and the confined charge limits the Banbury mixer to small batches. The production rate is increased as much as possible by using powerful drives and rotating the blades at the highest speed that the material will stand. The friction produced in the confined space is great, and with heat-sensitive materials cooling may be the limiting factor. Recent innovations include a drop door, four-wing rotors which can provide 30 percent greater power than the older two-wing rotors, and separable gear housings. Equipment is available from laboratory size to a mixer capable of handling a 450-kg (1000-lb) charge and applying 2240 kW (3000 hp).

High-Intensity Mixer. Mixers such as that shown in Fig. 18-44 combine a high shear zone with a fluidized vortex mixing action. Blades at the bottom of the vessel scoop the batch upward at peripheral speeds of about 40 m/s (130 ft/s). The high shear stress (to 20,000 s^{-1}) and blade impact easily reduce agglomerates and aid intimate dispersion. Since the energy input is high [200 kW/m^3 (about 8 hp/ft^3)], even powdery material is heated rapidly.

Mixers of this type are available in sizes from 4 to 2000 L (1 to 500 gal), consuming from 1.5 to 375 kW (2 to 500 hp).

These mixers are particularly suited for rapid mixing of powders and granules with liquids, for dissolving resins or solids in liquids, or for removal of volatiles from pastes under vacuum. Scale-up is usually on the basis of maintaining constant peripheral velocity of the impeller.

Roll Mills Roll mills can provide exceedingly high localized shear while retaining extended surface for temperature control.

Two-Roll Mills These mills contain two parallel rolls mounted in a heavy frame with provision for accurately regulating the pressure and distance between the rolls. As one pass between the rolls does little blending and only a small amount of work, the mills are practically always used as batch mixers. Only a small amount of material is in the high-shear zone at any one time.

To increase the wiping action, the rolls are usually operated at different speeds. The material passing between the rolls is returned to the feed point by the rotation of the rolls. If the rolls are at different temperatures, the material usually will stick to the hotter roll and return to the feed point as a thick layer.

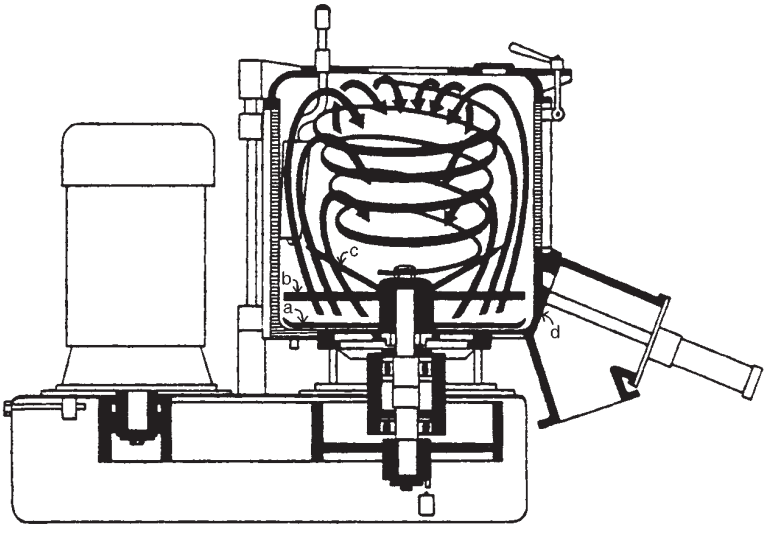


FIG. 18-44 High-intensity mixer: (*a*) bottom scraper; (*b*) fluidizing tool; (*c*) horn tool; (*d*) flush-mounted discharge valve. (*Henschel Mixers America, Inc.*)

At the end of the period of batch mixing, heavy materials may be discharged by dropping between the rolls, while thin mixes may be removed by a scraper bar pressing against the descending surface of one of the rolls.

Two-roll mills are used mainly for preparing color pastes for the ink, paint, and coating industries. There are a few applications in heavy-duty blending of rubber stocks, for which corrugated and masticating rolls are often used.

Miscellaneous Batch Mixers

Bulk Blenders Many of the mixers used for solids blending (Sec. 19) are also suitable for some liquid-solids blending. **Ribbon blenders** can be used for such tasks as wetting out or coating a powder. When the final paste product is not too fluid, other solids-handling equipment finds frequent use.

Plow Mixers Plow mixers such as the **Littleford** (Littleford Day) and the **Marion** (Rapids Machinery Co.) machines can be used for either batch or continuous mixing. Plow-shaped heads arranged on the horizontal shaft rotate at high speed, hurling the material throughout the free space of the vessel. Additional intermixing and blending occur as the impellers plow through the solids bed. Special high-speed choppers (3600 r/min) can be installed to break up lumps and aid liquid incorporation. The choppers also disperse fine particles throughout viscous materials to provide a uniform suspension. The mixer is available in sizes of 40 L to 40 m^3 (10 to 10,000 gal) of working capacity.

Cone and Screw Mixers The **Nauta mixer** of Fig. 18-45 (Day Mixing) utilizes an orbiting action of a helical screw rotating on its own axis to carry material upward, while revolving about the centerline of the cone-shaped shell near the wall for top-to-bottom circulation. Reversing the direction of screw rotation aids discharge of pasty materials. Partial batches are mixed in the Nauta type of mixer as efficiently as full loads. These mixers, available in sizes of 40 L to 40 m^3 (10 to 10,000 gal), achieve excellent low-energy blending, with some hydraulic shear dispersion. At constant speed, both mixing time and power scale up with the square root of volume.

Pan Muller Mixers These mixers can be used if the paste is not too fluid or too sticky. The main application of muller mixers is now in the foundry industry, in mixing small amounts of moisture and binder materials with sand particles for both core and molding sand. In paste processing, pan-and-plow mixers are used principally for mixing putty and clay pastes, while muller mixers handle such diversified materials as clay, storage-battery paste, welding-rod coatings, and chocolate coatings.

In muller mixers the rotation of the circular pan or of the plows brings the material progressively into the path of the mullers, where the intensive action takes place. Figure 18-46 shows one type of mixer, in which the mullers and plows revolve around a stationary turret in a stationary pan. The outside plow moves material from the crib wall to the path of the following muller; the inside plow moves it from the central turret to the path of the other muller. The mullers crush the material, breaking down lumps and aggregates.

Standard muller mixers range in capacity from a fraction of a cubic foot to more than 1.8 m^3 (60 ft^3), with power requirements ranging from 0.2 to 56 kW (⅓ to 75 hp). A continuous muller design employs two intersecting and communicating cribs, each with its own mullers and plows. At the point of intersection of the two crib bodies, the outside plows give an approximately equal exchange of material from one crib to the other, but material builds up in the first crib until the feed rate and the discharge rate of material from the gate in the second crib are equal. The residence time is regulated by adjusting the outlet gate.

CONTINUOUS MIXERS

Some of the batch mixers previously described can be converted for continuous processing. Product uniformity may be poor because of the broad residence time distribution. If the different ingredients can be accurately metered, various continuous mixers are available. Continuous mixers generally consist of a closely fitted agitator element rotating within a stationary housing.

Single-Screw Mixers Because of the growth of the plastics industry, use of extruders such as that depicted in Fig. 18-47 are now very widespread. The quality and usefulness of the product may well depend on how uniformly the various additives, stabilizers, fillers, etc., have been incorporated. The extruder combines the process functions of melting the base resin, mixing in the additives, and developing the pressure required for shaping the product into pellets, sheet, or profiles. Dry ingredients, sometimes premixed in a batch blender, are fed into the feed throat where the channel depth is deepest. As the root diameter of the screw is increased, the plastic is melted by a combination of friction and heat transfer from the barrel. Shear forces can be very high, especially in the melting zone, and the mixing is primarily a laminar shearing action.

Single-screw extruders can be built with a long length-to-diameter ratio to permit a sequence of process operations, such as staged addition of various ingredients. Capacity is determined by diameter, length, and power. Although the majority of extruders are in the 25- to 200-mm-diameter range, much larger units have been made for specific applications such as polyethylene homogenization. Mixing

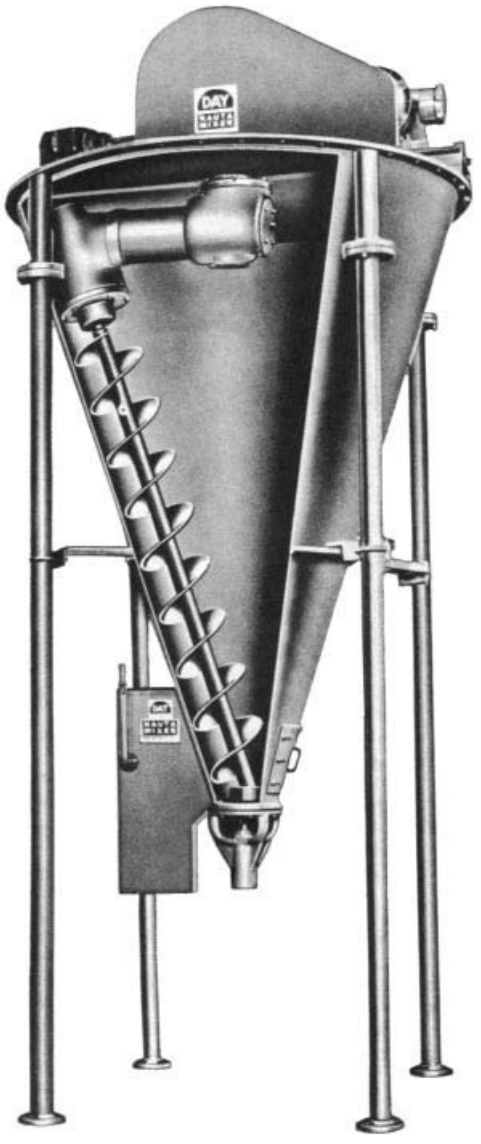


FIG. 18-45 Nauta mixer. (*Littleford Day.*)

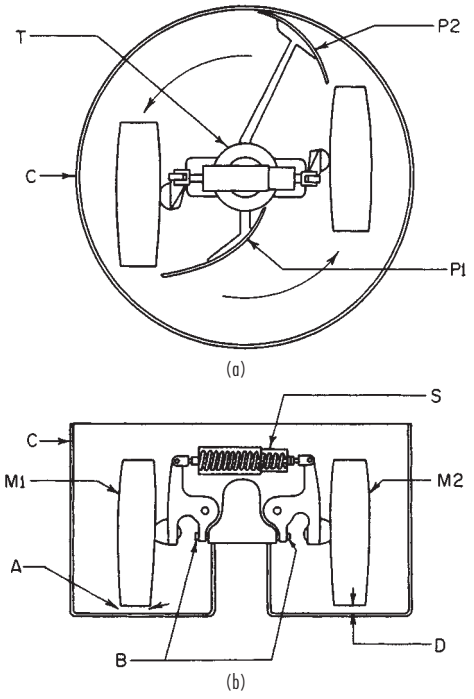


FIG. 18-46 Pan muller: (*a*) plan view; (*b*) sectional elevation. [*Bullock,* Chem. Eng. Prog. ***51:*** *243 (1955), by permission.*]

enhancers (Fig. 18-48) are utilized to provide both elongational reorienting and shearing action to provide for both dispersive and distributive mixing.

The maximum power (P, kW) being supplied for single-screw extruders varies with screw diameter (D, mm) approximately as follows:

$$P = 5.3 \times 10^{-3} D^{2.25}$$

The power required for most polymer mixing applications varies from 0.15 to 0.3 kWh/kg.

Rietz Extruder This extruder, shown schematically in Fig. 18-49, has orifice plates and baffles along the vessel. The rotor carries multiple blades with a forward pitch, generating the head for extrusion through the orifice plates as well as battering the material to break up agglomerates between the baffles. Typical applications include wet granulation of pharmaceuticals, blending color in bar soap, and mixing and extruding cellulose materials. The Extructor is available in rotor diameters up to 600 mm (24 in) and in a power range of 5 to 112 kW (7 to 150 hp).

Twin-Screw Extruders With two screws in a figure-eight barrel, advantage can be taken of the interaction between the screws as well as between the screw and the barrel. Twin-screw machines are used in continuous melting, mixing, and homogenizing of different polymers with various additives, or to carry out the intimate mixing required for reactions in which at least one of the components is of high viscosity. The screws can be tangential or intermeshing, and the latter either co- or counterrotating. Tangential designs allow variability in channel depth and permit longer lengths.

Counterrotating intermeshing screws provide a dispersive milling action between the screws and behave like a positive displacement device with the ability to generate pressure more efficiently than any other extruder.

The most common type of twin-screw mixing extruder is the corotating intermeshing variety (APV, Berstorff, Davis Standard, Leistritz, Werner & Pfleiderer). The two keyed or splined shafts are fitted with pairs of slip-on kneading or conveying elements, as shown in Fig. 18-50. The arrays of these elements can be varied to provide a wide range of mixing effects. The barrel sections are also segmented to allow for optimum positioning of feed ports, vents, barrel valves, etc. The barrels may be heated electrically or with oil or steam and cooled with air or water.

Each pair of kneading paddles causes an alternating compression and expansion effect which massages the contents and provides a combination of shearing and elongational mixing actions. The corotating twin-screw mixers are available in sizes ranging from 15 to 300 mm, with length-to-diameter ratios up to 50 and throughput capacities up to 25,000 kg/h. Screw speeds can be high (to 500 r/min in the smaller-production-size extruders), and residence times for mixing are usually under 2 min.

Farrel Continuous Mixer This mixer (Fig. 18-51) consists of rotors similar in cross section to the Banbury batch mixer. The first section of the rotor acts as a screw conveyor, propelling the feed ingredients to the mixing section. The mixing action is a combination of intensive shear, between rotor and chamber wall, kneading between the rotors, and a rolling action of the material itself. The amount and quality of mixing are controlled by adjustment of speed, feed rates, and discharge-orifice opening. Units are available in five sizes with mixing-chamber volumes ranging up to 0.12 m^3 (4.2 ft^3). At 200 r/min, the power range is 5 to 2200 kW (7 to 3000 hp).

Miscellaneous Continuous Mixers

Trough-and-Screw Mixers These mixers usually consist of single or twin rotors which continually turn the feed material over as it

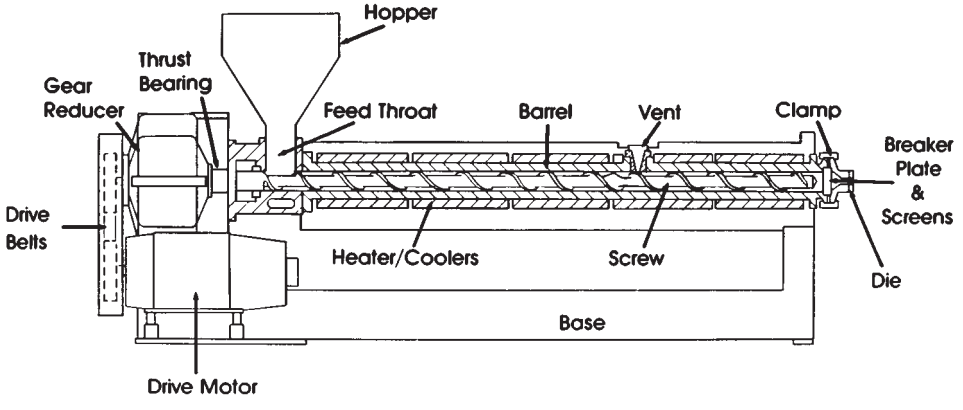


FIG. 18-47 Single-screw extruder. (*Davis Standard.*)

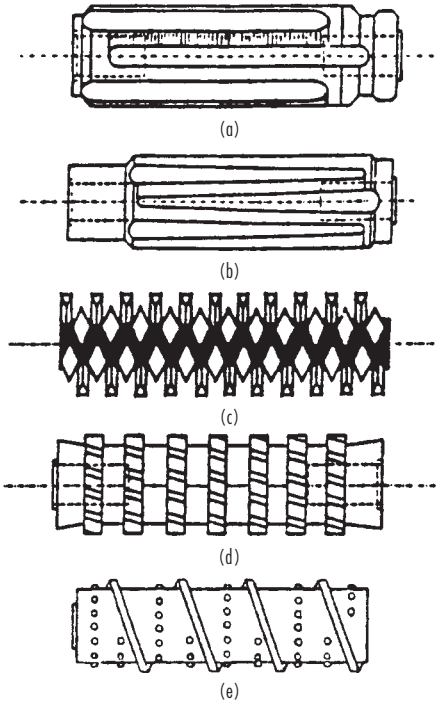


FIG. 18-48 Mixing enhancers for single-screw extruders: (*a*) Maddock (straight); (*b*) Maddock (tapered); (*c*) pineapple; (*d*) gear; (*e*) pin.

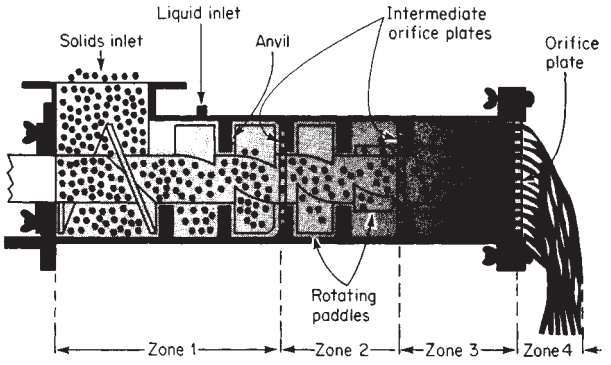


FIG. 18-49 Rietz Extruder. (*Bepex Corporation.*)

progresses toward the discharge end. Some have been designed with extensive heat-transfer area. The continuous-screw **Holo-Flite Processor** (Fig. 18-52; Denver Sala) is used primarily for heat transfer, since the hollow screws present extended surface without contributing much shear. Two or four screws may be used. Bethlehem Corp.'s **Porcupine Processor** also has heat-transfer media going through the flights of the rotor, but the agitator flights are cut to provide a folding action on the process mass. Breaker-bar assemblies, consisting of fingers extending toward the shaft, are frequently used to improve agitation.

Another type of trough-and-screw mixer with a large volume available for mixing is the AP Conti (List AG) machine shown in Fig. 18-53. These self-cleaning-type mixers are particularly appropriate when

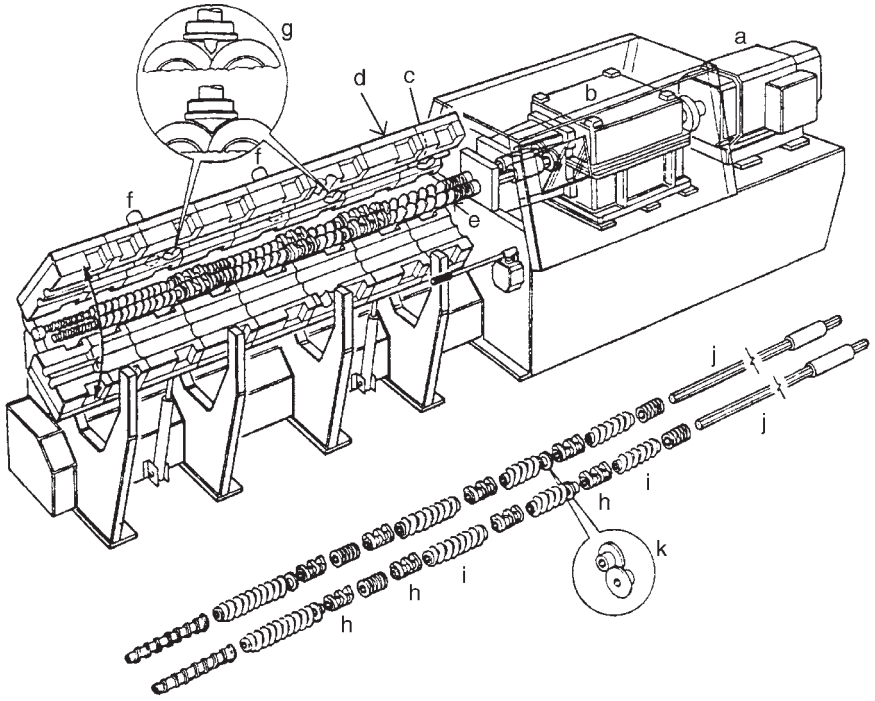


FIG. 18-50 Intermeshing corotating twin screw extruder: (*a*) drive motor; (*b*) gearbox; (*c*) feed port; (*d*) barrel; (*e*) assembled rotors; (*f*) vent; (*g*) barrel valve; (*h*) kneading paddles; (*i*) conveying screws; (*j*) splined shafts; (*k*) blister rings. (*APV Chemical Machinery, Inc.*)

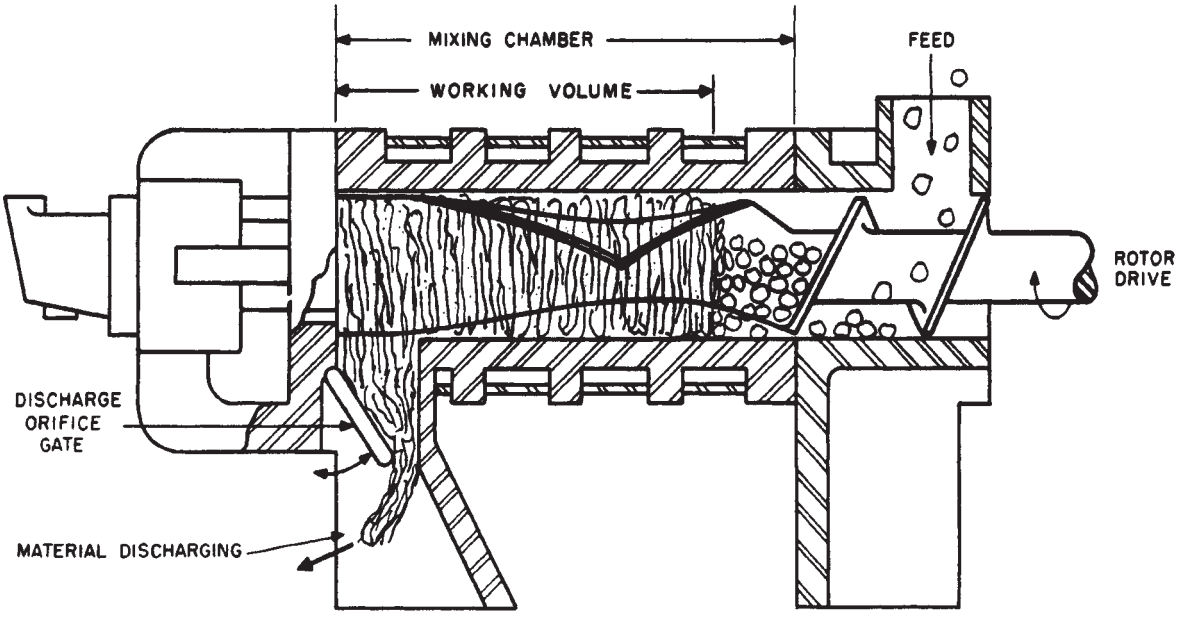


FIG. 18-51 Farrel continuous mixer. (*Farrel Co.*)

the product being handled goes through a sticky stage, which could plug the mixer or foul the heat-transfer surfaces.

Pug Mills A pug mill contains one or two shafts fitted with short, heavy paddles, mounted in a cylinder or trough which holds the material being processed. In two-shaft mills the shafts are parallel and may be horizontal or vertical. The paddles may or may not intermesh. Clearances are wide so that there is considerable mass mixing. Unmixed or partially mixed ingredients are fed at one end of the machine, which is usually totally enclosed. The paddles push the material forward as they cut through it, and carry the charge toward the discharge end as it is mixed. Product may discharge through one or two open ports or through one or more extrusion nozzles which give roughly shaped, continuous strips. Automatic cutters may be used to make blocks from the strips. Pug mills are most used for mixing mineral and clay products.

Kneadermaster This mixer (Patterson Industries, Inc.) is an adaptation of a sigma-blade mixer for continuous operation. Each two pairs of blades establish a mixing zone, the first pair pushing materials toward the discharge end of the trough and the second pair pushing them back. Forwarding to the next zone is by displacement with more feed material. Control of mixing intensity is by variation in rotor speed. Cored blades supplement the heat-transfer area of the jacketed trough.

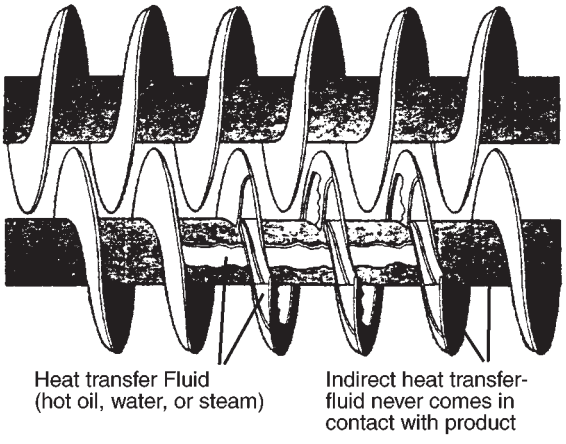


FIG. 18-52 Holo-Flite Processor. (*Denver Sala.*)

Motionless Mixers An alternative to agitated equipment for continuous viscous mixing involves the use of stationary shaped diverters inside conduits which force the fluid media to mix themselves through a progression of divisions and recombinations, forming striations of ever-decreasing thickness until uniformity is achieved. Simple diverters, such as the **Kenics static mixer** (Chemineer, Inc.; Fig. 18-54), provide 2^n layerings per n diverters.

The power consumed by a motionless mixer in producing the mixing action is simply that delivered by a pump to the fluid which it moves against the resistance of the diverter conduit. For a given rate of pumping, it is substantially proportional to that resistance. When the diverter consists of several passageways, as in the **Sulzer static mixer** (Koch Engineering Co., Inc.) shown in Fig. 18-55, the number of layerings (hence, the rate of mixing) per diverter is increased, but at the expense of a higher pressure drop. The pressure drop, usually expressed as a multiple K of that of the empty duct, is strongly dependent upon the hydraulic radius of the divided flow passageway. The value of K, obtainable from the mixer supplier, can range from 6 to several hundred, depending on the Reynolds number and the geometry of the mixer.

Motionless mixers continuously interchange fluid elements between the walls and the center of the conduit, thereby providing enhanced heat transfer and relatively uniform residence times. Distributive mixing is usually excellent; however, dispersive mixing may be poor, especially when viscosity ratios are high.

PROCESS DESIGN CONSIDERATIONS

Scaling Up Mixing Performance

Scale-Up of Batch Mixers The prime basis of scale-up of batch mixers has been equal power per unit volume, although the most desirable practical criterion is equal blending per unit time. As size is increased, mechanical-design requirements may limit the larger mixer to lower agitator speeds; if so, blend times will be longer in the larger

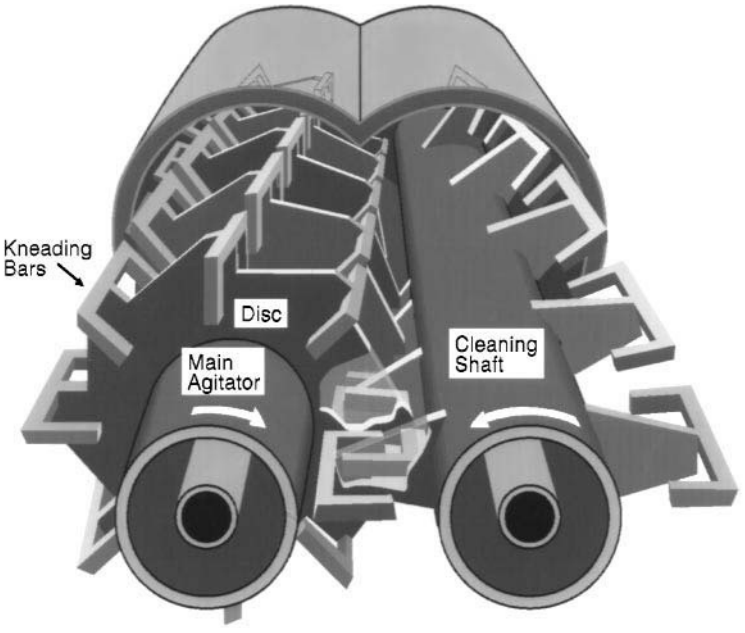


FIG. 18-53 AP Conti paste mixer. (*LIST.*)

mixer than in the smaller prototype. If the power is high, the lower surface-to-volume ratio as size is increased may make temperature buildup a limiting factor. Since the impeller in a paste mixer generally comes close to the vessel wall, it is not possible to add cooling coils. In some instances, the impeller blades can be cored for additional heat-transfer area.

Experience with double-arm mixers indicates that power is proportional to the product of blade radius, blade-wing depth, trough length, and average of the speeds of the two blades (Irving and Saxton, loc. cit.). The mixing time scales up inversely with blade speed. Goodness of mixing is dependent primarily on the number of revolutions that the blades have made. As indicated previously, the minimum possible mixing time may become dependent on heat-transfer rate.

Frequently, the physical properties of a paste vary considerably during the mixing cycle. Even if one knew exactly how power depended upon density and viscosity, it might be better to predict the requirements for a large paste mixer from the power-time curve observed in the prototype mixer rather than to try to calculate or measure all intermediate properties during the processing sequence (i.e., the prototype mixer may be the best instrument to use to measure the effective viscosity).

Scale-Up of Continuous Mixers Although scaling up on the basis of constant power per unit feed rate [kWh/kg or (hp·h)/lb] is usually a good first estimate, several other factors may have to be considered. As the equipment scale is increased, geometric similarity being at least approximated, there is a loss in surface-to-volume ratio. As size is increased, changing shear rate or length-to-diameter ratio may be required because of equipment-fabrication limitations. Furthermore, even if a reliable method of scaling up power exists, the determination of net power in small-scale test equipment is frequently difficult and inaccurate because of fairly large no-load power.

As a matter of fact, geometrical similarity usually cannot be maintained exactly as the size of the model is increased. In single-screw extruders, for example, channel depth in the flights cannot be increased in proportion to screw diameter because the distribution of heat generated by friction at the barrel wall requires more time as channel depth becomes greater. With constant retention time, therefore, nonhomogeneous product would be discharged from the scaled-up model. As the result of the departure from geometrical similarity, the throughput rate of single-screw extruders scales up with diameter



FIG. 18-54 Kenics static mixer. (*Chemineer, Inc.*)

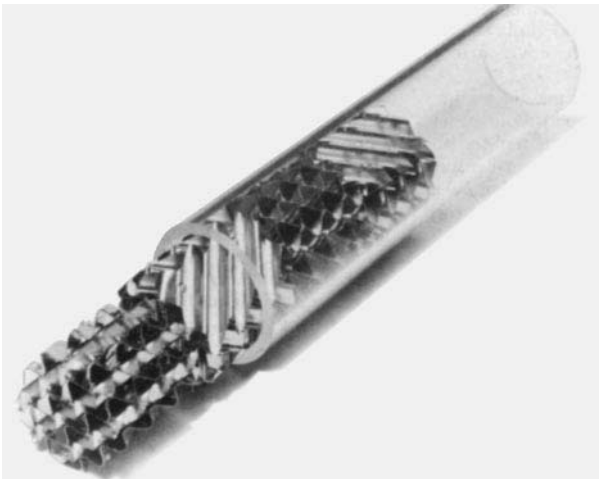


FIG. 18-55 Sulzer static mixer. (*Koch Engineering Co., Inc.*)

to the power 2.0 to 2.5 (instead of diameter cubed) at constant length-to-diameter ratio and screw speed.

The throughput rate of intermeshing twin-screw extruders (Fig. 18-56) and the Farrel continuous mixer (Fig. 18-51) is scaled up with diameter to about the 2.6 power.

If the process can be operated adiabatically, the production capacity is scaled up as the cube of diameter since geometry, shear rate, residence time, and power input per unit volume all can be held constant.

Residence-time distributions. For flow through a conduit, the extent of axial dispersion can be characterized either by an axial-diffusion coefficient or by analogy to a number of well-mixed stages in series. Retention time can control the performance of a mixing system. As the number of apparent stages increases, there is greater assurance that all the material will have the required residence time. Under conditions requiring uniform retention time, it is imperative that the feed streams be fed in the correct ratio on a time scale much shorter than the average residence time of the mixer; otherwise, a perturbation in the feed will produce a comparable perturbation in the product. The mixing impellers in continuous mixers can be designed to cover the full range from minimum axial mixing (plug flow) to maximum (to damp out feed irregularities). Residence-time distributions and effective Peclet numbers have been determined for a wide variety of twin-screw configurations [Todd and Irving, *Chem. Eng. Prog.*, **65**(9), 84 (1969)]. Conventional single-screw extruder mixers have Peclet numbers about equal to the length-to-diameter ratio, or an equivalent number of stages equal to one-half of that.

HEATING AND COOLING MIXERS

Heat Transfer Pastes are often heated or cooled by heat transfer through the walls of the container or hollow mixing arms. Good agitation, a large ratio of transfer surface to mixer volume, and frequent removal of material from the surface are essential for high rates of heat transfer. Sometimes evaporation of part of the mix is used for cooling.

In most mixers, the metal wall has a negligible thermal resistance. The paste film, however, usually has high resistance. It is important, therefore, while minimizing the resistance of the heating or cooling medium, to move the paste up to and away from the smooth wall surface as steadily and rapidly as possible. This is best achieved by having the paste flow so as to follow a close-fitting scraper which wipes the film from the wall with each rotation. Typical overall heat-transfer coefficients are between 25 and 200 J/(m^2·s·K) [4 to 35 Btu/(h·ft^2·°F)].

Heating Methods The most economical heating method varies with plant location and available facilities. Direct firing is rarely used, since it does not permit good surface-temperature control and may cause scorching of the material on the vessel walls. Steam heating is the most widely used method. It is economical, safe, and easily controlled. With thin-wall mixers there must be automatic release of the vacuum that results when the pressure is reduced and the steam in the jacket condenses; otherwise, weak sections will collapse. Transfer-liquid heating using water, oil, special organic liquids, or molten inorganic salts permits good temperature control and provides insurance against overheating the processed material. Jackets for transfer-liquid heating usually must be baffled to provide good circulation. Higher temperatures can be achieved without requiring the heavy vessel construction otherwise required by steam.

Electrical heating is accomplished with resistance bands or ribbons which must be electrically insulated from the machine body but in good thermal contact with it. The heaters must be carefully spaced to avoid a succession of hot and cold areas. Sometimes they are mounted in aluminum blocks shaped to conform to the container walls. Their effective temperature range is 150 to 500°C (about 300 to 930°F). Temperature control is precise, maintenance and supervision costs are low, and conversion of electrical energy to useful heat is almost 100 percent. The cost of electrical energy is usually large, however, and may be prohibitive.

Frictional heat develops rapidly in some units such as a Banbury mixer. The first temperature rise may be beneficial in softening the materials and accelerating chemical reactions. High temperatures detrimental to the product may easily be reached, however, and provision for cooling or frequent stopping of the machine must be made. Frictional heating may be lessened by reducing the number of working elements, their area, and their speed. Cooling thus is facilitated, but at the expense of increased mixing time.

Cooling Methods In air cooling, air may be blown over the machine surfaces, the area of which is best extended with fins. Air or cooled inert gas may also be blown over the exposed surface of the mix, provided contamination or oxidation of the charge does not result. Evaporation of excess water or solvent under vacuum or at atmospheric pressure provides good cooling. A small amount of evaporation produces a large amount of cooling. Removing too much solvent, however, may damage the charge. Direct addition of ice to the mixer provides rapid, convenient cooling, but the resulting dilution of the mix must be permissible. Addition of dry ice is more expensive but results in lower temperatures, the mix is not diluted, and the CO_2 gas evolved provides a good inert atmosphere. Many mixers are cooled by circulation of water or refrigerants through jackets or hollow agitators. In general, this is the least expensive method, but it is limited by the magnitude of heat-transfer coefficient obtainable.

Selection of Equipment If a new product is being considered, the preliminary study must be highly detailed. Laboratory or pilot-plant work must be done to establish the controlling factors. The problem is then to select and install equipment which will operate for quantity production at minimum overall cost. Most equipment vendors have pilot equipment available on a rental basis or can conduct test runs in their own customer-demonstration facilities.

One approach to proper equipment specification is by analogy. What current product is most similar to the new one? How is this material produced? What difficulties are being experienced?

In other situations the following procedure is recommended:

1. List carefully all materials to be handled at the processing point and describe their characteristics, such as:
   a. How received at the processing unit: in bags, barrels, or drums, in bulk, by pipe line, etc.?
   b. Must storage and/or weighing be done at the site?
   c. Physical form.
   d. Specific gravity and bulk characteristics.
   e. Particle size or size range.
   f. Viscosity.
   g. Melting or boiling point.
   h. Corrosive properties.
   i. Abrasive characteristics.
   j. Is material poisonous?
   k. Is material explosive?
   l. Is material an irritant to skin, eyes, or lungs?
   m. Is material sensitive to exposure of air, moisture, or heat?
2. List pertinent data covering production:
   a. Quantity to be produced per 8-h shift.
   b. Formulation of finished product.
   c. What accuracy of analysis is required?
   d. Will changes in color, flavor, odor, or grade require frequent cleaning of equipment?
   e. Is this operation independent, or does it serve other process stages with which it must be synchronized?
   f. Is there a change in physical state during processing?
   g. Is there a chemical reaction? Is it endothermic or exothermic?
   h. What are the temperature requirements?
   i. What is the form of the finished product?
   j. How must the material be removed from the apparatus (by pumping, free flow through pipe or chute, dumping, etc.)?
3. Describe in detail the controlling characteristics of the finished product:
   a. Permanence of the emulsion or dispersion.
   b. Degree of blending of aggregates or of ultimate particles.
   c. Ultimate color development required.
   d. Uniformity of the dispersion of active ingredients, as in a drug product.
   e. Degree of control of moisture content for pumping extrusion, and so on.

Preparation and Addition of Materials To ensure maximum production of high-grade mixed material, the preliminary preparation

of the ingredients must be correct and they must be added in the proper order. There are equipment implications to these considerations.

Some finely powdered materials, such as carbon black, contain much air. If possible they should be compacted or wet out before being added to the mix. If a sufficient quantity of light solvent is a part of the formula, it may be used to wet the powder and drive out the air. If the powder cannot be wet, it may be possible to densify it somewhat by mechanical means. Removal of adsorbed gas under vacuum is sometimes necessary.

Not uncommonly, critical ingredients that are present in small proportion (e.g., vulcanizers, antioxidants, and antiacids) tend to form aggregates when dry. Before entering the mixer, they should be fluffed, either by screening if the aggregates are soft or by passage through a hammer mill, roll mill, or muller if they are hard. The mixing time is cut down and the product is more uniform if all ingredients are freed from aggregates before mixing.

If any solids present in small amounts are soluble in a liquid portion of the mix, it is well to add them as a solution, making provision to distribute the liquid uniformly throughout the mass. When a trace of solid material which is not soluble in any other ingredients is to be added, it may be expedient to add it as a solution in a neutral solvent, with provision to evaporate the solvent at the end of the mixing cycle.

It may be advisable to consider master batching, in which a low-proportion ingredient is separately mixed with part of some other ingredient of the mix, this premix then being added to the rest of the mix for final dispersion. Master batching is especially valuable in adding tinting colors, antioxidants, and the like. The master batch may be made up with laboratory accuracy, while at the mixing station weighing errors are minimized by the dilution of the important ingredient.

Considerations such as these may make it desirable to consider automatic weighing and batch accumulation, metering of liquid ingredients, and automatic control of various time cycles.

CRYSTALLIZATION FROM SOLUTION

General References: *AIChE Testing Procedures: Crystallizers*, American Institute of Chemical Engineers, New York, 1970; *Evaporators*, 1961. Bennett, *Chem. Eng. Prog.*, **58**(9), 76 (1962). Buckley, *Crystal Growth*, Wiley, New York, 1951. Campbell and Smith, *Phase Rule*, Dover, New York, 1951. De Jong and Jancic (eds.), *Industrial Crystallization*, North-Holland Publishing Company, Amsterdam, 1979. "Crystallization from Solution: Factors Influencing Size Distribution," *Chem. Eng. Prog. Symp. Ser.*, **67**(110), (1971). Mullin (ed.), *Industrial Crystallization*, Plenum, New York, 1976. Newman and Bennett, *Chem. Eng. Prog.*, **55**(3), 65 (1959). Palermo and Larson (eds.), "Crystallization from Solutions and Melts," *Chem. Eng. Prog. Symp. Ser.*, **65**(95), (1969). Randolph (ed.), "Design, Control and Analysis of Crystallization Processes," *Am. Inst. Chem. Eng. Symp. Ser.*, **76**(193), (1980). Randolph and Larson, *Theory of Particulate Processes*, Academic, New York, 2d ed., 1988. Rousseau and Larson (eds.), "Analysis and Design of Crystallization Processes," *Am. Inst. Chem. Eng. Symp. Ser.*, **72**(153), (1976). Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, American Chemical Society, Washington, 1965. Myerson (ed.), *Handbook of Industrial Crystallization*, Butterworth, 1993.

Crystallization is important as an industrial process because of the number of materials that are and can be marketed in the form of crystals. Its wide use is probably due to the highly purified and attractive form of a chemical solid which can be obtained from relatively impure solutions in a single processing step. In terms of energy requirements, crystallization requires much less energy for separation than do distillation and other commonly used methods of purification. In addition, it can be performed at relatively low temperatures and on a scale which varies from a few grams up to thousands of tons per day.

Crystallization may be carried out from a vapor, from a melt, or from a solution. Most of the industrial applications of the operation involve crystallization from solutions. Nevertheless, crystal solidification of metals is basically a crystallization process, and much theory has been developed in relation to metal crystallization. This topic is so specialized, however, that it is outside the scope of this subsection, which is limited to crystallization from solution.

PRINCIPLES OF CRYSTALLIZATION

Crystals A crystal may be defined as a solid composed of atoms arranged in an orderly, repetitive array. The interatomic distances in a crystal of any definite material are constant and are characteristic of that material. Because the pattern or arrangement of the atoms is repeated in all directions, there are definite restrictions on the kinds of symmetry that crystals can possess.

There are five main types of crystals, and these types have been arranged into seven crystallographic systems based on the crystal interfacial angles and the relative length of its axes. The treatment of the description and arrangement of the atomic structure of crystals is the science of **crystallography.** The material in this discussion will be limited to a treatment of the growth and production of crystals as a unit operation.

Solubility and Phase Diagrams Equilibrium relations for crystallization systems are expressed in the form of solubility data which are plotted as phase diagrams or solubility curves. Solubility data are ordinarily given as parts by weight of anhydrous material per 100 parts by weight of total solvent. In some cases these data are reported as parts by weight of anhydrous material per 100 parts of solution. If water of crystallization is present in the crystals, this is indicated as a separate phase. The concentration is normally plotted as a function of temperature and has no general shape or slope. It can also be reported as a function of pressure, but for most materials the change in solubility with change in pressure is very small. If there are two components in solution, it is common to plot the concentration of these two components on the *X* and *Y* axes and represent the solubility by isotherms. When three or more components are present, there are various techniques for depicting the solubility and phase relations in both three-dimension and two-dimension models. For a description of these techniques, refer to Campbell and Smith (loc. cit.). Shown in Fig. 18-56 is a phase diagram for magnesium sulfate in water. The line *p–a* represents the freezing points of ice (water) from solutions of magne-

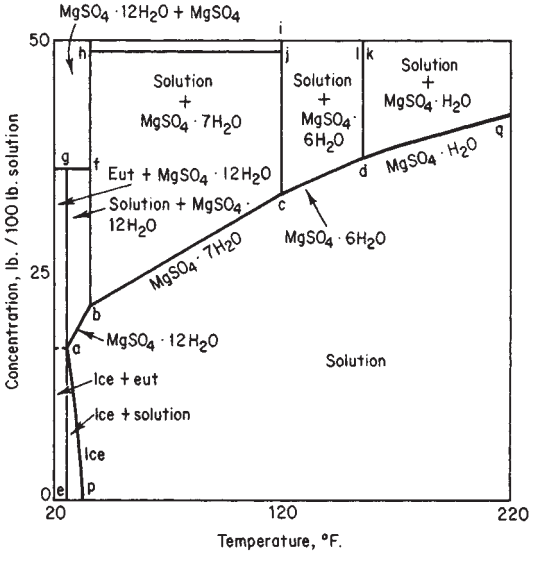


FIG. 18-56 Phase diagram. $MgSO_4 \cdot H_2O$. To convert pounds to kilograms, divide by 2.2; K = (°F + 459.7)/1.8.

sium sulfate. Point *a* is the eutectic, and the line *a–b–c–d–q* is the solubility curve of the various hydrates. Line *a–b* is the solubility curve for $MgSO_4 \cdot 12H_2O$, *b–c* is the solubility curve for $MgSO_4 \cdot 7H_2O$, *c–d* is the solubility curve for $MgSO_4 \cdot 6H_2O$, and *d–q* is the portion of the solubility curve for $MgSO_4 \cdot H_2O$.

As shown in Fig. 18-57, the mutual solubility of two salts can be plotted on the *X* and *Y* axes with temperatures as isotherm lines. In the example shown, all the solution compositions corresponding to 100°C with solid-phase sodium chloride present are shown on the line *DE*. All the solution compositions at equilibrium with solid-phase KCl at 100°C are shown by the line *EF*. If both solid-phase KCl and NaCl are present, the solution composition at equilibrium can only be represented by point *E*, which is the invariant point (at constant pressure). Connecting all the invariant points results in the mixed-salt line. The locus of this line is an important consideration in making phase separations.

There are numerous solubility data in the literature; the standard reference is by Seidell (loc. cit.). Valuable as they are, they nevertheless must be used with caution because the solubility of compounds is often influenced by pH and/or the presence of other soluble impurities which usually tend to depress the solubility of the major constituents. While exact values for any system are frequently best determined by actual composition measurements, the difficulty of reproducing these solubility diagrams should not be underestimated. To obtain data which are readily reproducible, elaborate pains must be taken to be sure the system sampled is at equilibrium, and often this means holding a sample at constant temperature for a period of from 1 to 100 h. While the published curves may not be exact for actual solutions of interest, they generally will be indicative of the shape of the solubility curve and will show the presence of hydrates or double salts.

Heat Effects in a Crystallization Process The heat effects in a crystallization process can be computed by two methods: (1) a heat balance can be made in which individual heat effects such as sensible heats, latent heats, and the heat of crystallization can be combined into an equation for total heat effects; or (2) an enthalpy balance can be made in which the total enthalpy of all leaving streams minus the total enthalpy of all entering streams is equal to the heat absorbed from external sources by the process. In using the heat-balance method, it is necessary to make a corresponding mass balance, since the heat effects are related to the quantities of solids produced through the heat of crystallization. The advantage of the enthalpy-concentration-diagram method is that both heat and mass effects are taken into account simultaneously. This method has limited use because of the difficulty in obtaining enthalpy-concentration data. This information has been published for only a few systems.

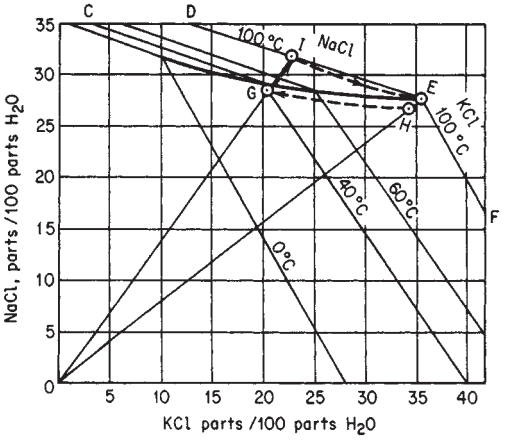


FIG. 18-57 Phase diagram, KCl – NaCl – H_2O. K = °C + 273.2.

With compounds whose solubility increases with increasing temperature there is an absorption of heat when the compound dissolves. In compounds with decreasing solubility as the temperature increases, there is an evolution of heat when solution occurs. When there is no change in solubility with temperature, there is no heat effect. The solubility curve will be continuous as long as the solid substance of a given phase is in contact with the solution, and any sudden change in the slope of the curve will be accompanied by a change in the heat of solution and a change in the solid phase. Heats of solution are generally reported as the change in enthalpy associated with the dissolution of a large quantity of solute in an excess of pure solvent. Tables showing the heats of solution for various compounds are given in Sec. 2.

At equilibrium the heat of crystallization is equal and opposite in sign to the heat of solution. Using the heat of solution at infinite dilution as equal but opposite in sign to the heat of crystallization is equivalent to neglecting the heat of dilution. With many materials the heat of dilution is small in comparison with the heat of solution and the approximation is justified; however, there are exceptions. Relatively large heat effects are usually found in the crystallization of hydrated salts. In such cases the total heat released by this effect may be a substantial portion of the total heat effects in a cooling-type crystallizer. In evaporative-type crystallizers the heat of crystallization is usually negligible when compared with the heat of vaporizing the solvent.

Yield of a Crystallization Process In most cases the process of crystallization is slow, and the final mother liquor is in contact with a sufficiently large crystal surface so that the concentration of the mother liquor is substantially that of a saturated solution at the final temperature in the process. In such cases it is normal to calculate the yield from the initial solution composition and the solubility of the material at the final temperature. If evaporative crystallization is involved, the solvent removed must be taken into account in determining the final yield. If the crystals removed from solution are hydrated, account must be taken of the water of crystallization in the crystals, since this water is not available for retaining the solute in solution. The yield is also influenced in most plants by the removal of some mother liquor with the crystals being separated from the process. Typically, with a product separated on a centrifuge or filter, the adhering mother liquor would be in the range of 2 to 10 percent of the weight of the crystals.

The actual yield may be obtained from algebraic calculations or trial-and-error calculations when the heat effects in the process and any resultant evaporation are used to correct the initial assumptions on calculated yield. When calculations are made by hand, it is generally preferable to use the trial-and-error system, since it permits easy adjustments for relatively small deviations found in practice, such as the addition of wash water, or instrument and purge water additions. The following calculations are typical of an evaporative crystallizer precipitating a hydrated salt. If SI units are desired, kilograms = pounds × 0.454; K = (°F + 459.7)/1.8.

Example 1: Yield from a Crystallization Process A 10,000-lb batch of a 32.5 percent $MgSO_4$ solution at 120°F is cooled without appreciable evaporation to 70°F. What weight of $MgSO_4 \cdot 7H_2O$ crystals will be formed (if it is assumed that the mother liquor leaving is saturated)?

From the solubility diagram in Fig. 18-56 at 70°F the concentration of solids is 26.3 lb $MgSO_4$ per 100-lb solution.

The mole weight of $MgSO_4$ is 120.38.

The mole weight of $MgSO_4 \cdot 7H_2O$ is 246.49.

For calculations involving hydrated salts, it is convenient to make the calculations based on the hydrated solute and the "free water."

$$0.325 \text{ weight fraction} \times \frac{246.94}{120.38} = 0.6655 \text{ } MgSO_4 \cdot 7H_2O \text{ in the feed solution}$$

$$0.263 \times \frac{246.94}{120.38} = 0.5385 \text{ } MgSO_4 \cdot 7H_2O \text{ in the mother liquor}$$

Since the free water remains constant (except when there is evaporation), the final amount of soluble $MgSO_4 \cdot 7H_2O$ is calculated by the ratio of

$$\frac{0.538 \text{ lb } MgSO_4 \cdot 7H_2O}{(1 - 0.538) \text{ lb free water}}$$

	Total	$MgSO_4 \cdot 7H_2O$	Free water	$\frac{MgSO_4 \cdot 7H_2O}{\text{Free water}}$
Feed	10,000	6655	3345	1.989
Mother liquor	7249	3904*	3345	1.167
Yield	2751	2751		

*3345 × (0.538/0.462) = 3904

A formula method for calculation is sometimes used where

$$P = R\,\frac{100W_0 - S(H_0 - E)}{100 - S(R - 1)}$$

where P = weight of crystals in final magma, lb
R = mole weight of hydrate/mole weight of anhydrous = 2.04759
S = solubility at mother-liquor temperature (anhydrous basis) in lb per 100 lb solvent. [0.263/(1 − 0.263)] × 100 = 35.68521
W_0 = weight of anhydrous solute in the original batch. 10,000(0.325) = 3250 lb
H_0 = total weight of solvent at the beginning of the batch. 10,000 − 3250 = 6750 lb
E = evaporation = 0

$$P = 2.04\,\frac{(100)(3250) - 35.7(6750)}{100 - 35.7(2.04 - 1)} = 2751 \text{ lb}$$

Note that taking the difference between large numbers in this method can increase the chance for error.

Fractional Crystallization When two or more solutes are dissolved in a solvent, it is often possible to (1) separate these into the pure components or (2) separate one and leave the other in the solution. Whether or not this can be done depends on the solubility and phase relations of the system under consideration. Normally alternative 2 is successful only when one of the components has a much more rapid change in solubility with temperature than does the other. A typical example which is practiced on a large scale is the separation of KCl and NaCl from water solution. A phase diagram for this system is shown in Fig. 18-57. In this case the solubility of NaCl is plotted on the Y axis in parts per 100 parts of water, and the solubility of KCl is plotted on the X axis. The isotherms show a marked decrease in solubility for each component as the amount of the other is increased. This is typical for most inorganic salts. As explained earlier, the mixed-salt line is CE, and to make a separation of the solutes into the pure components it is necessary to be on one side of this line or the other. Normally a 95 to 98 percent approach to this line is possible. When evaporation occurs during a cooling or concentration process, this can be represented by movement away from the origin on a straight line through the origin. Dilution by water is represented by movement in the opposite direction.

A typical separation might be represented as follows: Starting at E with a saturated brine at 100°C a small amount of water is added to dissolve any traces of solid phase present and to make sure the solids precipitated initially are KCl. Evaporative cooling along line HG results in the precipitation of KCl. During this evaporative cooling, part of the water evaporated must be added back to the solution to prevent the coprecipitation of NaCl. The final composition at G can be calculated by the NaCl/KCl/H_2O ratios and the known amount of NaCl in the incoming solution at E. The solution at point G may be concentrated by evaporation at 100°C. During this process the solution will increase in concentration with respect to both components until point I is reached. Then NaCl will precipitate, and the solution will become more concentrated in KCl, as indicated by the line IE, until the original point E is reached. If concentration is carried beyond point E, a mixture of KCl and NaCl will precipitate.

Example 2: Yield from Evaporative Cooling Starting with 1000 lb of water in a solution at H on the solubility diagram in Fig. 18-57, calculate the yield on evaporative cooling and concentrate the solution back to point H so the cycle can be repeated, indicating the amount of NaCl precipitated and the evaporation and dilution required at the different steps in the process.

In solving problems of this type, it is convenient to list the material balance and the solubility ratios. The various points on the material balance are calculated by multiplying the quantity of the component which does not precipitate from solution during the transition from one point to another (normally the NaCl in cooling or the KCl in the evaporative step) by the solubility ratio at the next step, illustrated as follows:

Basis. 1000 lb of water at the initial conditions.

				Solubility ratios		
Solution component	KCl	NaCl	Water	KCl	NaCl	Water
H	343	270	1000	34.3	27.0	100
$G(a)$	194	270	950	20.4	28.4	100
KCl yield	149					
Net evaporation			50			
$I(b)$	194	270	860	22.6	31.4	100
$E(c)$	194	153	554	35.0	27.5	100
NaCl yield		117				
Evaporation			306			
Dilution			11			
H'	194	153	565	34.3	27.0	−100

The calculations for these steps are:

a. 270 lb NaCl (100 lb water/28.4 lb NaCl) = 950 lb water
950 lb water (20.4 lb KCl/100 lb water) = 194 lb KCl
b. 270 lb NaCl (100 lb water/31.4 lb NaCl) = 860 lb water
860 lb water (22.6 lb KCl/100 lb water) = 194 lb KCl
c. 194 lb KCl (100 lb water/35.0 lb KCl) = 554 lb water
554 lb water (27.5 lb NaCl/100 lb water) = 153 lb NaCl

Note that during the cooling step the maximum amount of evaporation which is permitted by the material balance is 50 lb for the step shown. In an evaporative-cooling step, however, the actual evaporation which results from adiabatic cooling is more than this. Therefore, water must be added back to prevent the NaCl concentration from rising too high; otherwise, coprecipitation of NaCl will occur.

Inasmuch as only mass ratios are involved in these calculations, kilograms or any other unit of mass may be substituted for pounds without affecting the validity of the example.

Although the figures given are for a step-by-step process, it is obvious that the same techniques will apply to a continuous system if the fresh feed containing KCl and NaCl is added at an appropriate part of the cycle, such as between steps G and I for the case of dilute feed solutions.

Another method of fractional crystallization, in which advantage is taken of different crystallization rates, is sometimes used. Thus, a solution saturated with borax and potassium chloride will, in the absence of borax seed crystals, precipitate only potassium chloride on rapid cooling. The borax remains behind as a supersaturated solution, and the potassium chloride crystals can be removed before the slower borax crystallization starts.

Crystal Formation There are obviously two steps involved in the preparation of crystal matter from a solution. The crystals must first form and then grow. The formation of a new solid phase either on an inert particle in the solution or in the solution itself is called **nucleation.** The increase in size of this nucleus with a layer-by-layer addition of solute is called **growth.** Both nucleation and crystal growth have supersaturation as a common driving force. Unless a solution is supersaturated, crystals can neither form nor grow. Supersaturation refers to the quantity of solute present in solution compared with the quantity which would be present if the solution were kept for a very long period of time with solid phase in contact with the solution. The latter value is the equilibrium solubility at the temperature and pressure under consideration. The supersaturation coefficient can be expressed

$$S = \frac{\text{parts solute/100 parts solvent}}{\text{parts solute at equilibrium/100 parts solvent}} \geqq 1.0 \qquad (18\text{-}22)$$

Solutions vary greatly in their ability to sustain measurable amounts of supersaturation. With some materials, such as sucrose, it is possible to develop a supersaturation coefficient of 1.4 to 2.0 with little danger of nucleation. With some common inorganic solutions such as sodium chloride in water, the amount of supersaturation which can be generated stably is so small that it is difficult or impossible to measure.

Certain qualitative facts in connection with supersaturation, growth, and the yield in a crystallization process are readily apparent.

If the concentration of the initial solution and the final mother liquor are fixed, the total weight of the crystalline crop is also fixed if equilibrium is obtained. The particle-size distribution of this weight, however, will depend on the relationship between the two processes of nucleation and growth. Considering a given quantity of solution cooled through a fixed range, if there is considerable nucleation initially during the cooling process, the yield will consist of many small crystals. If only a few nuclei form at the start of the precipitation and the resulting yield occurs uniformly on these nuclei without secondary nucleation, a crop of large uniform crystals will result. Obviously, many intermediate cases of varying nucleation rates and growth rates can also occur, depending on the nature of the materials being handled, the rate of cooling, agitation, and other factors.

When a process is continuous, nucleation frequently occurs in the presence of a seeded solution by the combined effects of mechanical stimulus and nucleation caused by supersaturation (heterogeneous nucleation). If such a system is completely and uniformly mixed (i.e., the product stream represents the typical magma circulated within the system) and if the system is operating at steady state, the particle-size distribution has definite limits which can be predicted mathematically with a high degree of accuracy, as will be shown later in this section.

Geometry of Crystal Growth Geometrically a crystal is a solid bounded by planes. The shape and size of such a solid are functions of the interfacial angles and of the linear dimension of the faces. As the result of the constancy of its interfacial angles, each face of a growing or dissolving crystal, as it moves away from or toward the center of the crystal, is always parallel to its original position. This concept is known as the "principle of the parallel displacement of faces." The rate at which a face moves in a direction perpendicular to its original position is called the translation velocity of that face or the rate of growth of that face.

From the industrial point of view, the term **crystal habit** or **crystal morphology** refers to the relative sizes of the faces of a crystal. The crystal habit is determined by the internal structure and external influences on the crystal such as the growth rate, solvent used, and impurities present during the crystallization growth period. The crystal habit of commercial products is of very great importance. Long, needlelike crystals tend to be easily broken during centrifugation and drying. Flat, platelike crystals are very difficult to wash during filtration or centrifugation and result in relatively low filtration rates. Complex or twinned crystals tend to be more easily broken in transport than chunky, compact crystal habits. Rounded or spherical crystals (caused generally by attrition during growth and handling) tend to give considerably less difficulty with caking than do cubical or other compact shapes.

Internal structure can be different in crystals that are chemically identical, even though they may be formed at different temperatures and have a different appearance. This is called **polymorphism** and can be determined only by X-ray diffraction. For the same internal structure, very small amounts of foreign substances will often completely change the crystal habit. The selective adsorption of dyes by different faces of a crystal or the change from an alkaline to an acidic environment will often produce pronounced changes in the crystal habit. The presence of other soluble anions and cations often has a similar influence. In the crystallization of ammonium sulfate, the reduction in soluble iron to below 50 ppm of ferric ion is sufficient to cause significant change in the habit of an ammonium sulfate crystal from a long, narrow form to a relatively chunky and compact form. Additional information is available in the patent literature and Table 18-4 lists some of the better-known additives and their influences.

Since the relative sizes of the individual faces of a crystal vary between wide limits, it follows that different faces must have different translational velocities. A geometric law of crystal growth known as the **overlapping principle** is based on those velocity differences: in growing a crystal, only those faces having the lowest translational velocities survive; and in dissolving a crystal, only those faces having the highest translational velocities survive.

For example, consider the cross sections of a growing crystal as in Fig. 18-58. The polygons shown in the figure represent varying stages in the growth of the crystal. The faces marked *A* are slow-growing faces (low translational velocities), and the faces marked *B* are fast-growing (high translational velocities). It is apparent from Fig. 18-58 that the faster *B* faces tend to disappear as they are overlapped by the slower *A* faces.

Hartman and Perdok (1955) predicted that crystal habit or crystal morphology was related to the internal structure based on energy considerations and speculated it should be possible to predict the growth shape of crystals from the slice energy of different flat faces. Later, Hartman was able to predict the calculated attachment energy for various crystal species. Recently computer programs have been developed that predict crystal morphology from attachment energies. These techniques are particularly useful in dealing with organic or molecular crystals and rapid progress in this area is being made by companies such as Molecular Simulations of Cambridge, England.

Purity of the Product If a crystal is produced in a region of the phase diagram where a single-crystal composition precipitates, the crystal itself will normally be pure provided that it is grown at relatively low rates and constant conditions. With many products these purities approach a value of about 99.5 to 99.8 percent. The difference between this and a purity of 100 percent is generally the result of small pockets of mother liquor called occlusions trapped within the crystal. Although frequently large enough to be seen with an ordinary microscope, these occlusions can be submicroscopic and represent dislocations within the structure of the crystal. They can be caused by either attrition or breakage during the growth process or by slip planes within the crystal structure caused by interference between screw-type dislocations and the remainder of the crystal faces. To increase the purity of the crystal beyond the point where such occlusions are normally expected (about 0.1 to 0.5 percent by volume), it is generally necessary to reduce the impurities in the mother liquor itself to an acceptably low level so that the mother liquor contained within these occlusions will not contain sufficient impurities to cause an impure product to be formed. It is normally necessary to recrystallize material from a solution which is relatively pure to surmount this type of purity problem.

In addition to the impurities within the crystal structure itself, there is normally an adhering mother-liquid film left on the surface of the crystal after separation in a centrifuge or on a filter. Typically a centrifuge may leave about 2 to 10 percent of the weight of the crystals as adhering mother liquor on the surface. This varies greatly with the size and shape or habit of the crystals. Large, uniform crystals precipitated from low-viscosity mother liquors will retain a minimum of mother liquor, while nonuniform or small crystals precipitated from viscous solutions will retain a considerably larger proportion. Comparable statements apply to the filtration of crystals, although normally the amounts of mother liquor adhering to the crystals are considerably larger. It is common practice when precipitating materials from solutions which contain appreciable quantities of impurities to wash the crystals on the centrifuge or filter with either fresh solvent or feed solution. In principle, such washing can reduce the impurities quite substantially. It is also possible in many cases to reslurry the crystals in fresh solvent and recentrifuge the product in an effort to obtain a longer residence time during the washing operation and better mixing of the wash liquors with the crystals.

Coefficient of Variation One of the problems confronting any user or designer of crystallization equipment is the expected particle-size distribution of the solids leaving the system and how this distribution may be adequately described. Most crystalline-product distributions plotted on arithmetic-probability paper will exhibit a straight line for a considerable portion of the plotted distribution. In this type of plot the particle diameter should be plotted as the ordinate and the cumulative percent on the log-probability scale as the abscissa.

It is common practice to use a parameter characterizing crystal-size distribution called the coefficient of variation. This is defined as follows:

$$CV = 100 \frac{PD_{16\%} - PD_{84\%}}{2PD_{50\%}} \qquad (18\text{-}23)$$

where CV = coefficient of variation, as a percentage
PD = particle diameter from intercept on ordinate axis at percent indicated

TABLE 18-4 Some Impurities Known to Be Habit Modifiers

Material crystallized	Additive(s)	Effect	Concentration	References
$Ba(NO_2)^2$	Mg, Te^{+4}	Helps growth	—	1
$CaSO_4 \cdot 2H_2O$	Citric, succinic, tartaric acids	Helps growth	Low	
	Sodium citrate	Forms prisms	—	5
$CuSO_4 \cdot 5H_2O$	H_2SO_4	Chunky crystals	0.3%	5
KCl	$K_4Fe(CN)_6$	Inhibits growth, dendrites	1000 ppm	4
	Pb, Bi, Sn^{+2}, Ti, Zr, Th, Cd, Fe, Hg, Mg	Helps growth	Low	1
$KClO_4$	Congo red (dye)	Modifies the 102 face	50 ppm	6
K_2CrO_4	Acid magenta (dye)	Modifies the 010 face	50 ppm	6
KH_2PO_4	$Na_2B_4O_7$	Aids growth	—	1
KNO_2	Fe	Helps growth	Low	1
KNO_3	Acid magenta (dye)	Tabular crystals		7
	Pb, Th, Bi	Helps growth	Low	1
K_2SO_4	Acid magenta (dye)	Forms plates	2000 ppm	6
	Cl, Mn, Mg, Bi, Cu, Al, Fe	Helps growth	Low	1
	Cl_3	Reduces growth rate	1000 ppm	4
	$(NH_4)_3Ce(NO_3)_6$	Reduces growth rate	1000 ppm	4
$LiCl \cdot H_2O$	$Cr \cdot Mn^{+2}$, Sn^{+2}, Co, Ni, Fe^{+3}	Helps growth	Low	1
$MgSO_4 \cdot 7H_2O$	Borax	Aids growth	5%	1
$Na_2B_4O_7 \cdot 10H_2O$	Sodium oleate	Reduces growth & nuc.	5 ppm	
	Casein, gelatin	Promotes flat crystals	—	2, 5
	NaOH, Na_2CO_3	Promotes chunky crystals	—	
$Na_2CO_3 \cdot H_2O$	$SO_4^=$	Reduces *L/D* ratio	0.1–1.0%	Canadian Patent 812,685
	Ca^{+2} and Mg^{+2}	Increase bulk density	400 ppm	U.S. Patent 3,459,497
$NaCO_3 \cdot NaHCO_3 \cdot 2H_2O$	D-40 detergent	Aids growth	20 ppm	U.S. Patent 3,233,983
NaCl	$Na_4Fe(CN)_6$, CdBr	Forms dendrites	100 ppm	4
	Pb, Mn^{+2}, Bi, Sn^{+2}, Ti, Fe, Hg	Helps growth	Low	1
	Urea, formamide	Forms octahedra	Low	2
	Tetraalkyl ammon. salts	Helps growth & hardness	1–100 ppm	U.S. Patent 3,095,281
	Polyethylene-oxy compounds	Helps growth & hardness	—	U.S. Patent 3,000,708
$NaClO_3$	Na_2SO_4, $NaClO_4$	Tetrahedrons	—	3
$NaNO_3$	Acid green (dye)	Flattened rhombahedra		7
Na_2SO_4	NH_4SO_4 @ pH 6.5	Large single crystals	Low	
	$CdCl_2$	Inhibits growth	1000 ppm	4
	Alkyl aryl sulfonates	Aids growth	—	2
	Calgon	Aids growth	100 ppm	
NH_4Cl	Mn, Fe, Cu, Co, Ni, Cr	Aid growth	Low	1
	Urea	Forms octahedra		5
NH_4ClO_4	Azurine (dye)	Modifies the 102 face	22 ppm	6
NF_4F	Ca	Helps growth	Low	1
$(NH_4)NO_3$	Acid magenta (dye)	Forms 010 face plates	1%	6
$(NH_4)_2HPO_4$	H_2SO_4	Reduces *L/D* ratio	7%	
$NH_4H_2PO_4$	Fe^{+3}, Cr, Al, Sn	Helps growth	Traces	1
$(NH_4)_2SO_4$	Cr^{+3}, Fe^{+3}, Al^{+3}	Promotes needles	50 ppm	
	H_2SO_4	Promotes needles	2–6%	U.S. Patent 2,092,073
	Oxalic acid, citric acid	Promotes chunky crystals	1000 ppm	U.S. Patent 2,228,742
	H_3PO_4, SO_2	Promotes chunky crystals	1000 ppm	
$ZnSO_4 \cdot 7H_2O$	Borax	Aids growth	—	1
Adipic acid	Surfactant-SDBS	Aids growth	50–100 ppm	2
Fructose	Glucose, difructose	Affects growth		8
L-asparagine	L-glutamic acid	Affects growth		8
Naphthalene	Cyclohexane (solvent)	Forms needles	—	2
	Methanol (solvent)	Forms plates		
Pentaerythritol	Sucrose	Aids growth	—	1
	Acetone (solvent)	Forms plates	—	2
Sodium glutamate	Lysine, CaO	Affects growth		8
Sucrose	Raffinose, KCl, NaBr	Modify growth rate		
Urea	Biuret	Reduces *L/D* & aids growth	2–7%	
	NH_4Cl	Reduces *L/D* & aids growth	5–10%	

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6. Buckley, *Crystal Growth,* (Faraday Soc.) Butterworths, 1949, p. 249.
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8. Nyvlt, J., *Industrial Crystallization,* Verlag Chemie Publishers, New York, 1978, pp. 26–31.

In order to be consistent with normal usage, the particle-size distribution when this parameter is used should be a straight line between approximately 10 percent cumulative weight and 90 percent cumulative weight. By giving the coefficient of variation and the mean particle diameter, a description of the particle-size distribution is obtained which is normally satisfactory for most industrial purposes. If the product is removed from a mixed-suspension crystallizer, this coefficient of variation should have a value of approximately 50 percent (Randolph and Larson, op. cit., chap. 2).

Crystal Nucleation and Growth

Rate of Growth Crystal growth is a layer-by-layer process, and since growth can occur only at the face of the crystal, material must be transported to that face from the bulk of the solution. Diffusional

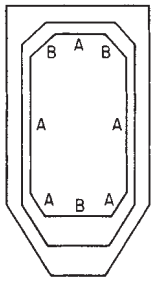


FIG. 18-58 Overlapping principle.

resistance to the movement of molecules (or ions) to the growing crystal face, as well as the resistance to integration of those molecules into the face, must be considered. As discussed earlier, different faces can have different rates of growth, and these can be selectively altered by the addition or elimination of impurities.

If L is a characteristic dimension of a crystal of selected material and shape, the rate of growth of a crystal face that is perpendicular to L is, by definition,

$$G \equiv \lim_{\Delta L \to O} \frac{\Delta L}{\Delta t} = \frac{dL}{dt} \tag{18-24}$$

where G is the growth rate over time internal t. It is customary to measure G in the practical units of millimeters per hour. It should be noted that growth rates so measured are actually twice the facial growth rate.

The delta L *law.* It has been shown by McCabe [*Ind. Eng. Chem.*, **21,** 30, 112 (1929)] that all geometrically similar crystals of the same material suspended in the same solution grow at the same rate if growth rate is defined as in Eq. (18-24). The rate is independent of crystal size, provided that all crystals in the suspension are treated alike. This generalization is known as the delta L law. Although there are some well-known exceptions, they usually occur when the crystals are very large or when movement of the crystals in the solution is so rapid that substantial changes occur in diffusion-limited growth of the faces.

It is emphasized that the delta L law does not apply when similar crystals are given preferential treatment based on size. It fails also when surface defects or dislocations significantly alter the growth rate of a crystal face. Nevertheless, it is a reasonably accurate generalization for a surprising number of industrial cases. When it is, it is important because it simplifies the mathematical treatment in modeling real crystallizers and is useful in predicting crystal-size distribution in many types of industrial crystallization equipment.

Important exceptions to McCabe's growth-rate model have been noted by Bramson, by Randolph, and by Abegg. These are discussed by Canning and Randolph, *Am. Inst. Chem. Eng. J.,* **13,** 5 (1967).

Nucleation The mechanism of crystal nucleation from solution has been studied by many scientists, and recent work suggests that—in commercial crystallization equipment, at least—the nucleation rate is the sum of contributions by (1) homogeneous nucleation and (2) nucleation due to contact between crystals and (*a*) other crystals, (*b*) the walls of the container, and (*c*) the pump impeller. If B^0 is the net number of new crystals formed in a unit volume of solution per unit of time,

$$B^0 = B_{ss} + B_e + B_c \tag{18-25}$$

where B_e is the rate of nucleation due to crystal-impeller contacts, B_c is that due to crystal-crystal contacts, and B_{ss} is the homogeneous nucleation rate due to the supersaturation driving force. The mechanism of the last-named is not precisely known, although it is obvious that molecules forming a nucleus not only have to coagulate, resisting the tendency to redissolve, but also must become oriented into a fixed lattice. The number of molecules required to form a stable crystal nucleus has been variously estimated at from 80 to 100 (with ice), and the probability that a stable nucleus will result from the simultaneous collision of that large number is extremely low unless the supersaturation level is very high or the solution is supersaturated in the absence of agitation. In commercial crystallization equipment, in which supersaturation is low and agitation is employed to keep the growing crystals suspended, the predominant mechanism is contact nucleation or, in extreme cases, attrition.

In order to treat crystallization systems both dynamically and continuously, a mathematical model has been developed which can correlate the nucleation rate to the level of supersaturation and/or the growth rate. Because the growth rate is more easily determined and because nucleation is sharply nonlinear in the regions normally encountered in industrial crystallization, it has been common to assume

$$B^0 = ks^i \tag{18-26}$$

where s, the supersaturation, is defined as $(C - C_s)$, C being the concentration of the solute and C_s its saturation concentration; and the exponent i and dimensional coefficient k are values characteristic of the material.

While Eq. (18-26) has been popular among those attempting correlations between nucleation rate and supersaturation, recently it has become commoner to use a derived relationship between nucleation rate and growth rate by assuming that

$$G = k's \tag{18-27}$$

whence, in consideration of Eq. (18-26),

$$B^0 = k''G^i \tag{18-28}$$

where the dimensional coefficient k' is characteristic of the material and the conditions of crystallization and $k'' = k/(k')^i$. Feeling that a model in which nucleation depends only on supersaturation or growth rate is simplistically deficient, some have proposed that contact nucleation rate is also a power function of slurry density and that

$$B^0 = k_n G^i M_T^j \tag{18-29}$$

where M_T is the density of the crystal slurry, g/L.

Although Eqs. (18-28) and (18-29) have been adopted by many as a matter of convenience, they are oversimplifications of the very complex relationship that is suggested by Eq. (18-25); Eq. (18-29) implicitly and quite arbitrarily combines the effects of homogeneous nucleation and those due to contact nucleation. They should be used only with caution.

In work pioneered by Clontz and McCabe [*Chem. Eng. Prog. Symp. Ser.,* **67**(110), 6 (1971)] and subsequently extended by others, contact nucleation rate was found to be proportional to the input of energy of contact, as well as being a function of contact area and supersaturation. This observation is important to the scaling up of crystallizers: at laboratory or bench scale, contact energy level is relatively low and homogeneous nucleation can contribute significantly to the total rate of nucleation; in commercial equipment, on the other hand, contact energy input is intense and contact nucleation is the predominant mechanism. Scale-up modeling of a crystallizer, therefore, must include its mechanical characteristics as well as the physiochemical driving force.

Nucleation and Growth From the preceding, it is clear that no analysis of a crystallizing system can be truly meaningful unless the simultaneous effects of nucleation rate, growth rate, heat balance, and material balance are considered. The most comprehensive treatment of this subject is by Randolph and Larson (op. cit), who developed a mathematical model for continuous crystallizers of the mixed-suspension or circulating-magma type [*Am. Inst. Chem. Eng. J.,* **8,** 639 (1962)] and subsequently examined variations of this model that include most of the aberrations found in commercial equipment. Randolph and Larson showed that when the total number of crystals in a given volume of suspension from a crystallizer is plotted as a function of the characteristic length as in Fig. 18-59, the slope of the line is usefully identified as the crystal population density, n:

$$n = \lim_{\Delta L \to O} \frac{\Delta N}{\Delta L} = \frac{dN}{dL} \tag{18-30}$$

where N = total number of crystals up to size L per unit volume of magma. The population density thus defined is useful because it char-

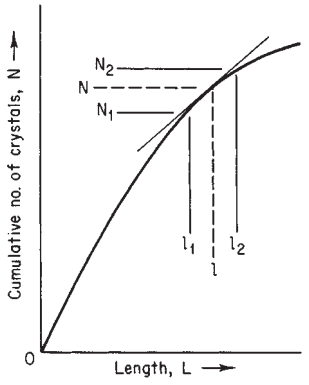


FIG. 18-59 Determination of the population density of crystals.

acterizes the nucleation-growth performance of a particular crystallization process or crystallizer.

The data for a plot like Fig. 18-60 are easily obtained from a screen analysis of the total crystal content of a known volume (e.g., a liter) of magma. The analysis is made with a closely spaced set of testing sieves, as discussed in Sec. 19, Table 19-6, the cumulative number of particles smaller than each sieve in the nest being plotted against the aperture dimension of that sieve. The fraction retained on each sieve is weighed, and the mass is converted to the equivalent number of particles by dividing by the calculated mass of a particle whose dimension is the arithmetic mean of the mesh sizes of the sieve on which it is retained and the sieve immediately above it.

In industrial practice, the size-distribution curve usually is not actually constructed. Instead, a mean value of the population density for any sieve fraction of interest (in essence, the population density of the particle of average dimension in that fraction) is determined directly as $\Delta N/\Delta L$, ΔN being the number of particles retained on the sieve and ΔL being the difference between the mesh sizes of the retaining sieve and its immediate predecessor. It is common to employ the units of $(\text{mm}\cdot\text{L})^{-1}$ for n.

For a steady-state crystallizer receiving solids-free feed and containing a well-mixed suspension of crystals experiencing negligible breakage, a material-balance statement degenerates to a particle balance (the Randolph-Larson general-population balance); in turn, it simplifies to

$$\frac{dn}{dL} + \frac{n}{Gt} = 0 \tag{18-31}$$

if the delta L law applies (i.e., G is independent of L) and the drawdown (or retention) time is assumed to be invariant and calculated as $t = V/Q$. Integrated between the limits n^0, the population density of nuclei (for which L is assumed to be zero), and n, that of any chosen crystal size L, Eq. (18-31) becomes

$$\int_{n^0}^{n} \frac{dn}{n} = -\int_0^L \frac{dL}{Gt} \tag{18-32}$$

$$\ln n = \frac{-L}{Gt} + \ln n^0 \tag{18-33a}$$

or

$$n = n^0 e^{-L/Gt} \tag{18-33b}$$

A plot of $\ln n$ versus L is a straight line whose intercept is $\ln n^0$ and whose slope is $-1/Gt$. (For plots on base-10 log paper, the appropriate slope correction must be made.) Thus, from a given product sample of known slurry density and retention time it is possible to obtain the nucleation rate and growth rate for the conditions tested if the sample satisfies the assumptions of the derivation and yields a straight line. A number of derived relations which describe the nucleation rate, size distribution, and average properties are summarized in Table 18-5.

If a straight line does *not* result (Fig. 18-60), at least part of the explanation may be violation of the delta L law (Canning and Randolph, loc. cit.). The best current theory about what causes size-dependent growth suggests what has been called growth dispersion or "Bujacian behavior" [Mullen (ed.), op. cit., p. 23]. In the same environment different crystals of the same size can grow at different rates owing to differences in dislocations or other surface effects. The graphs of "slow" growers (Fig. 18-60, curve *A*) and "fast" growers (curve *B*) sum to a resultant line (curve *C*), concave upward, that is described by Eq. (18-34) (Randolph, in deJong and Jancic, op. cit., p. 295):

$$n = \sum \frac{B^0 i}{G_i} e^{(-L/Git)} \tag{18-34}$$

Equation (18-31) contains no information about the crystallizer's influence on the nucleation rate. If the crystallizer is of a mixed-suspension, mixed-product-removal (MSMPR) type, satisfying the criteria for Eq. (18-31), and if the model of Clontz and McCabe is valid, the contribution to the nucleation rate by the circulating pump can be calculated [Bennett, Fiedelman, and Randolph, *Chem. Eng. Prog.*, **69**(7), 86 (1973)]:

$$B_e = K_e \left(\frac{I^2}{P}\right) \rho G \int_0^\infty nL^4\, dL \tag{18-35}$$

where I = tip speed of the propeller or impeller, m/s
ρ = crystal density, g/cm^3
P = volume of crystallizer/circulation rate (turnover), m^3/(m^3/s) = s

Since the integral term is the fourth moment of the distribution (m_4), Eq. (18-35) becomes

$$B_e = K_e \rho G \left(\frac{I^2}{P}\right) m_4 \tag{18-36}$$

Equation (18-36) is the general expression for impeller-induced nucleation. In a fixed-geometry system in which only the speed of the circulating pump is changed and in which the flow is roughly proportional to the pump speed, Eq. (18-36) may be satisfactorily replaced with

$$B_e = K_e'' \rho G (S_R)^3 m_4 \tag{18-37}$$

where S_R = rotation rate of impeller, r/min. If the maximum crystal-impeller impact stress is a nonlinear function of the kinetic energy, shown to be the case in at least some systems, Eq. (18-37) no longer applies.

In the specific case of an MSMPR exponential distribution, the fourth moment of the distribution may be calculated as

$$m_4 = 4! n^0 (Gt)^5 \tag{18-38}$$

Substitution of this expression into Eq. (18-36) gives

$$B_e = k n^0 G (S_R)^3 L_D^5 \tag{18-39}$$

where $L_D = 3Gt$, the dominant crystal (mode) size.

Equation (18-39) displays the competing factors that stabilize secondary nucleation in an operating crystallizer when nucleation is due mostly to impeller-crystal contact. Any increase in particle size produces a fifth-power increase in nucleation rate, tending to counteract the direction of the change and thereby stabilizing the crystal-size distribution. From dimensional argument alone the size produced in a mixed crystallizer for a (fixed) nucleation rate varies as $(B^0)^{1/3}$. Thus, this fifth-order response of contact nucleation does not wildly upset the crystal size distribution but instead acts as a stabilizing feedback effect.

Nucleation due to crystal-to-crystal contact is greater for equal striking energies than crystal-to-metal contact. However, the viscous drag of the liquid on particle sizes normally encountered limits the velocity of impact to extremely low values. The assumption that only the largest crystal sizes contribute significantly to the nucleation rate by crystal-to-crystal contact permits a simple computation of the rate:

$$B_c = K_c \rho G m_j^2 \tag{18-40}$$

where m_j = the fourth, fifth, sixth, or higher moments of the distribution.

A number of different crystallizing systems have been investigated by using the Randolph-Larson technique, and some of the published

TABLE 18-5 Common Equations for Population-Balance Calculations

Name	Symbol	Units	Systems without fines removal	Systems with fines removal		References
				Fines stream	Product stream	
Drawdown time (retention time)	t	h	$t = V/Q$	$t_F = V_{\text{liquid}}/Q_F$	$t = V/Q$	
Growth rate	G	mm/h	$G = dL/dt$	$G = dL/dt$	$G = dL/dt$	
Volume coefficient	K_v	1/no. (crystals)	$K_v = \dfrac{\text{volume of one crystal}}{L^3}$	$K_v = \dfrac{\text{volume of one crystal}}{L^3}$	$K_v = \dfrac{\text{volume of one crystal}}{L^3}$	
Population density	n	No. (crystals)/mm	$n = dN/dL$	$n = dN/dL$	$n = dN/dL$	1
Nuclei population density	n^o	No. (crystals)/mm	$n^o = K_M M^j G^{i-1}$			2
Population density	n	No. (crystals)/mm	$n = n^o e^{-L/Gt}$	$n_F = n^o e^{-L/Gt_F}$	$n = n^{o-L_c/Gt_F} e^{-L/Gt}$	1, 3
Nucleation rate	B_0	No. (crystals)/h	$B_0 = Gn^o = K_M M^j G^i$	$B_0 = G n_a^o$		4
Dimensionless length	x	None	$x = \dfrac{L}{Gt}$	$x_F = \dfrac{L}{Gt_F}$, $L_0 \rightarrow L_f$	$x = \dfrac{L}{Gt}$, $L_f \rightarrow L$	1
Mass/unit volume (slurry density)	M_T	g/L	$M_t = K_v \rho \int_0^\infty nL^3\,dL$ $M_t = K_v \rho 6\, n^o (Gt)^4$	$M_{T_F} = K_v \rho \int_0^{L_f} n^o e^{-L/Gt_F}\ L^3\,dL$	$M_T = K_v \rho \int_{L_f}^\infty n^o e^{-L/Gt_F} e^{-L/Gt}\, L^3\,dL$	1
$\dfrac{\text{Cumulative mass to } x}{\text{Total mass}}$	W_x	None	$W_x = 1 - e^{-x}\left(\dfrac{x^3}{6} + \dfrac{x^2}{2} + x + 1\right)$	$W_F = \dfrac{e^{-x}(x^3 + 3x^2 + 6x + 6) - 6}{e^{-x_c}(x_c^3 + 3x_c^2 + 6x_c + 6) - 6}$	$W = \dfrac{6K_v \rho n^o e^{-L_c/Gt_F} (Gt)^4 \left[1 - e^{-x}\left(\dfrac{x^3}{6} + \dfrac{x^2}{2} + x + 1\right)\right]}{\text{Slurry density } M,\ g/L}$ when $L_c \approx 0$, compared with L_a	5
Dominant particle	L_d	mm	$I_d = 3Gt$			
Average particle, weight	L_a	mm	$I_a = 3.67Gt$			6
Total number of crystals	N_T	No./L	$N_T = \int_0^\infty n\ dl$	$N_F = \int_0^{L_f} n_F\ dL$	$N_T = \int_{L_f}^\infty n\ dL$	1, 3

1. Randolph and Larson, *Am. Inst. Chem. Eng. J.,* **8,** 639 (1962).
2. Timm and Larson, *Am. Inst. Chem. Eng. J.,* **14,** 452 (1968).
3. Larson, private communication.
4. Larson, Timm, and Wolff, *Am. Inst. Chem. Eng. J.,* **14,** 448 (1968).
5. Larson and Randolph, *Chem. Eng. Prog. Symp. Ser.,* **65**(95), 1 (1969).
6. Schoen, *Ind. Eng. Chem.,* **53,** 607 (1961).

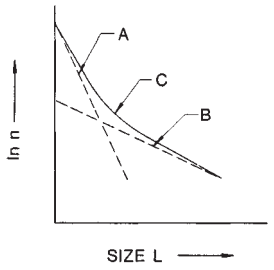


FIG. 18-60 Population density of crystals resulting from Bujacian behavior.

growth rates and nucleation rates are included in Table 18-6. Although the usefulness of these data is limited to the conditions tested, the table gives a range of values which may be expected, and it permits resolution of the information gained from a simple screen analysis into the fundamental factors of growth rate and nucleation rate. Experiments may then be conducted to determine the independent effects of operation and equipment design on these parameters.

Although this procedure requires laborious calculations because of the number of samples normally needed, these computations and the determination of the best straight-line fit to the data are readily programmed for digital computers.

Example 3: Population, Density, Growth and Nucleation Rate Calculate the population density, growth, and nucleation rates for a crystal sample of urea for which there is the following information. These data are from Bennett and Van Buren [*Chem. Eng. Prog. Symp. Ser.,* **65**(95), 44 (1969)].

Slurry density = 450 g/L
Crystal density = 1.335 g/cm^3
Drawdown time t = 3.38 h
Shape factor k_v = 1.00

Product size:

–14 mesh, +20 mesh	4.4 percent
–20 mesh, +28 mesh	14.4 percent
–28 mesh, +35 mesh	24.2 percent
–35 mesh, +48 mesh	31.6 percent
–48 mesh, +65 mesh	15.5 percent
–65 mesh, +100 mesh	7.4 percent
–100 mesh	2.5 percent

n = number of particles per liter of volume
14 mesh = 1.168 mm, 20 mesh = 0.833 mm, average opening 1.00 mm
Size span = 0.335 mm = ΔL

$$n_{20} = \frac{(450\text{ g/L})(0.044)}{(1.335/1000)\text{ g/mm}^3(1.00^3\text{ mm}^3\text{/particle})(0.335\text{ mm})(1.0)}$$

$$n_{20} = 44{,}270$$

$$\ln n_{20} = 10{,}698$$

Repeating for each screen increment:

Screen size	Weight, %	k_v	ln n	L, average diameter, mm
100	7.4	1.0	18.099	0.178
65	15.5	1.0	17.452	0.251
48	31.6	1.0	16.778	0.356
35	24.2	1.0	15.131	0.503
28	14.4	1.0	13.224	0.711
20	4.4	1.0	10.698	1.000

Plotting ln n versus L as shown in Fig. 18-61, a straight line having an intercept at zero length of 19.781 and a slope of –9.127 results. As mentioned in discussing Eq. (18-24), the growth rate can then be found.

$$\text{Slope} = -1/Gt \text{ or } -9.127 = -1/[G(3.38)]$$

or $$G = 0.0324\text{ mm/h}$$

and $$B_0 = Gn^0 = (0.0324)(e^{19.781}) = 12.65 \times 10^6\ \frac{n^0}{\text{L·h}}$$

and $$L_a = 3.67(0.0324)(3.38) = 0.40\text{ mm}$$

An additional check can be made of the accuracy of the data by the relation

$$M_T = 6k_v\rho n^0(Gt)^4 = 450\text{ g/L}$$

$$M_T = (6)(1.0)\frac{1.335\text{ g/cm}^3}{1000\text{ mm}^3\text{/cm}^3}\,e^{19.78}[(0.0324)(3.38)]^4$$

$$M_T = 455\text{ g/L} \approx 450\text{ g/L}$$

Had only the growth rate been known, the size distribution of the solids could have been calculated from the equation

$$W_f = 1 - e^{-x}\left(\frac{x^3}{6} + \frac{x^2}{2} + x + 1\right)$$

where W_f is the weight fraction *up to* size L and $x = L/Gt$.

$$x = \frac{L}{(0.0324)(3.38)} = \frac{L}{0.1095}$$

Screen size	L, mm	x	W_f^*	Cumulative % retained 100 $(1 - W_f)$	Measured cumulative % retained
20	0.833	7.70	0.944	5.6	4.4
28	0.589	5.38	0.784	21.6	18.8
35	0.417	3.80	0.526	47.4	43.0
48	0.295	2.70	0.286	71.4	74.6
65	0.208	1.90	0.125	87.5	90.1
100	0.147	1.34	0.048	95.2	97.5

*Values of W_f as a function of x may be obtained from a table of Wick's functions.

Note that the calculated distribution shows some deviation from the measured values because of the small departure of the actual sample from the theoretical coefficient of variation (i.e., 47.5 versus 52 percent).

Here it can be seen that the nucleation rate is a decreasing function of growth rate (and supersaturation). The physical explanation is believed to be the mechanical influence of the crystallizer on the growing suspension and/or the effect of Bujacian behavior.

Had sufficient data indicating a change in n^0 for various values of M at constant G been available, a plot of ln n^0 versus ln M at corresponding G's would permit determination of the power j.

Crystallizers with Fines Removal In Example 3, the product was from a forced-circulation crystallizer of the MSMPR type. In many cases, the product produced by such machines is too small for commercial use; therefore, a separation baffle is added within the crystallizer to permit the removal of unwanted fine crystalline material from the magma, thereby controlling the population density in the machine so as to produce a coarser crystal product. When this is done, the product sample plots on a graph of ln n versus L as shown in line P, Fig. 18-62. The line of steepest slope, line F, represents the particle-size distribution of the fine material, and samples which show this distribution can be taken from the liquid leaving the fines-separation baffle. The product crystals have a slope of lower value, and typically there should be little or no material present smaller than L_f, the size which the baffle is designed to separate. The effective nucleation rate for the product material is the intersection of the extension of line P to zero size.

As long as the largest particle separated by the fines-destruction baffle is small compared with the mean particle size of the product, the seed for the product may be thought of as the particle-size distribution corresponding to the fine material which ranges in length from zero to L_f, the largest size separated by the baffle.

The product discharged from the crystallizer is characterized by the integral of the distribution from size L_f to infinity:

$$M_T = k_v\rho \int_{L_f}^{\infty} n^0 \exp(-L_f/Gt_f) \exp(L/GT)\, L^3\, dL \qquad (18\text{-}41)$$

The integrated form of this equation is shown in Table 18-5.

For a given set of assumptions it is possible to calculate the characteristic curves for the product from the crystallizer when it is operated at various levels of fines removal as characterized by L_f. This has been done for an ammonium sulfate crystallizer in Fig. 18-63. Also shown in that figure is the actual size distribution obtained. In calculating theoretical size distributions in accordance with the Eq. (18-41), it is

TABLE 18-6 Growth Rates and Kinetic Equations for Some Industrial Crystallized Products

Material crystallized	G, m/s × 10^8	Range t, h	Range M_T, g/L	Temp., °C	Scale*	Kinetic equation for B_0 no./(L·s)	References†
$(NH_4)_2SO_4$	1.67	3.83	150	70	P	$B_0 = 6.62 \times 10^{-25} G^{0.82} p^{-0.92} m_2^{2.05}$	Bennett and Wolf, *AIChE,* SFC, 1979.
$(NH_4)_2SO_4$	0.20	0.25	38	18	B	$B_0 = 2.94(10^{10}) G^{1.03}$	Larsen and Mullen, *J. Crystal Growth* **20:** 183 (1973).
$(NH_4)_2SO_4$	—	0.20	—	34	B	$B_0 = 6.14(10^{-11}) S_R^{7.84} M_T^{0.98} G^{1.22}$	Youngquist and Randolph, *AIChE J.* **18:** 421 (1972).
$MgSO_4 \cdot 7H_2O$	3.0–7.0	—	—	25	B	$B_0 = 9.65(10^{12}) M_T^{0.67} G^{1.24}$	Sikdar and Randolph, *AIChE J.* **22:** 110 (1976).
$MgSO_4 \cdot 7H_2O$	—	—	Low	29	B	$B_0 = f\ (N, L^4, N^{4.2}, S^{2.5})$	Ness and White, *AIChE Symposium Series 153,* vol. 72, p. 64.
KCl	2–12	—	200	32	P	$B_0 = 7.12(10^{39}) M_T^{0.14} G^{4.99}$	Randolph et al., *AIChE J.* **23:** 500 (1977).
KCl	3.3	1–2	100	37	B	$B_0 = 5.16(10^{22}) M_T^{0.91} G^{2.77}$	Randolph et al., *Ind. Eng. Chem. Proc. Design Dev.* **20:** 496 (1981).
KCl	0.3–0.45	—	50–147	25–68	B	$B_0 = 5 \times 10^{-3} G^{2.78} (M_T TIP^2)^{1.2}$	Qian et al., *AIChE J.* **33**(10): 1690 (1987).
KCr_2O_7	1.2–9.1	0.25–1	14–42	—	B	$B_0 = 7.33(10^4) M_T^{0.6} G^{0.5}$	Desari et al., *AIChE J.* **20:** 43 (1974).
KCr_2O_7	2.6–10	0.15–0.5	20–100	26–40	B	$B_0 = 1.59(10^{-3}) S_R^3 M_T G^{0.48}$	Janse, Ph.D. thesis, Delft Technical University, 1977.
KNO_3	8.13	0.25–0.050	10–40	20	B	$B_0 = 3.85(10^{16}) M_T^{0.5} G^{2.06}$	Juraszek and Larson, *AIChE J.* **23:** 460 (1977).
K_2SO_4	—	0.03–0.17	1–7	30	B	$B_0 = 2.62(10^3) S_R^{2.5} M_T^{0.5} G^{0.54}$	Randolph and Sikdar, *Ind. Eng. Chem. Fund.* **15:** 64 (1976).
K_2SO_4	2–6	0.25–1	2–20	10–50	B	$B_0 = 4.09(10^6) \exp\left(\frac{10900}{RT}\right) M_T G^{0.5}$	Jones, Budz, and Mullin, *AIChE J.* **33:** 12 (1986).
K_2SO_4	0.8–1.6	—	—	—	B	$\frac{G}{G_0} = 1 + 2L^{2/3}$ (L in μm)	White, Bendig, and Larson, *AIChE Mtg.,* Washington, D.C., Dec. 1974.
NaCl	4–13	0.2–1	25–200	50	B	$B_0 = 1.92(10^{10}) S_R^2 M_T G^2$	Asselbergs, Ph.D. thesis, Delft Technical University, 1978.
NaCl	—	0.6	35–70	55	P	$B_0 = 8 \times 10^{10} N^2 G^2 M_T$	Grootscholten et al., *Chem. Eng. Design* **62:** 179 (1984).
NaCl	0.5	1–2.5	70–190	72	P	$B_0 = 1.47(10^2)\left(\frac{I^2}{P}\right) m_4^{0.84} G^{0.98}$	Bennett et al., *Chem. Eng. Prog.* **69**(7): 86 (1973).
Citric acid	1.1–3.7	—	—	16–24	B	$B_0 = 1.09(10^{10}) m_4^{0.084} G^{0.84}$	Sikdar and Randolph, *AIChE J.* **22:** 110 (1976).
Fructose	0.1–0.25	—	—	50	B	—	Shiau and Berglund, *AIChE J.* **33:** 6 (1987).
Sucrose	—	—	—	80	B	$B_0 = 5 \times 10^6 N^{0.7} M_T^{0.3} G^{0.4}$	Berglund and deJong, *Separations Technology* **1:** 38 (1990).
Sugar	2.5–5	0.375	50	45	B	$B_0 = 4.38(10^6) M_T^{1.01} (\Delta C - 0.5)^{1.42}$	Hart et al., *AIChE Symposium Series 193,* vol. 76, 1980.
Urea	0.4–4.2	2.5–6.8	350–510	55	P	$B_0 = 5.48(10^{-1}) M_T^{-3.87} G^{1.66}$	Bennett and Van Buren, *Chem. Eng. Prog. Symposium Series* **95**(7): 65 (1973).
Urea	—	—	—	3–16	B	$B_0 = 1.49(10^{-31}) S_R^{2.3} M_T^{1.07} G^{-3.54}$	Lodaya et al., *Ind. Eng. Chem. Proc. Design Dev.* **16:** 294 (1977).

*B = bench scale; P = pilot plant.
†Additional data on many components are in Garside and Shah, *Ind. Eng. Chem. Proc. Design Dev.,* **19,** 509 (1980).

assumed that the growth rate is a constant, whereas in fact larger values of L_f will interact with the system driving force to raise the growth rate and the nucleation rate. Nevertheless, Fig. 18-63 illustrates clearly the empirical result of the operation of such equipment, demonstrating that the most significant variable in changing the particle-size distribution of the product is the size removed by the baffle. Conversely, changes in retention time for a given particle-removal size L_f make a relatively small change in the product-size distribution.

It is implicit that increasing the value of L_f will raise the supersaturation and growth rate to levels at which mass homogeneous nucleation can occur, thereby leading to periodic upsets of the system or cycling [Randolph, Beer, and Keener, *Am. Inst. Chem. Eng. J.,* **19,** 1140 (1973)]. That this could actually happen was demonstrated experimentally by Randolph, Beckman, and Kraljevich [*Am. Inst. Chem. Eng. J.,* **23,** 500 (1977)], and that it could be controlled dynamically by regulating the fines-destruction system was shown by Beckman and Randolph [ibid., (1977)]. Dynamic control of a crystallizer with a fines-destruction baffle and fine-particle-detection equipment employing a light-scattering (laser) particle-size-measurement instrument is described in U.S. Patent, 4,263,010 and 5,124,265.

CRYSTALLIZATION EQUIPMENT

Whether a vessel is called an evaporator or a crystallizer depends primarily on the criteria used in arriving at its sizing. In an evaporator of the salting-out type, sizing is done on the basis of vapor release. In a crystallizer, sizing is normally done on the basis of the volume required for crystallization or for special features required to obtain the proper product size. In external appearance, the vessels could be identical. Evaporators are discussed in Sec. 11.

In the discussion which follows, crystallization equipment has been classified according to the means of suspending the growing product. This technique reduces the number of major classifications and segregates those to which Eq. (18-31) applies.

Mixed-Suspension, Mixed-Product-Removal Crystallizers This type of equipment, sometimes called the circulating-magma

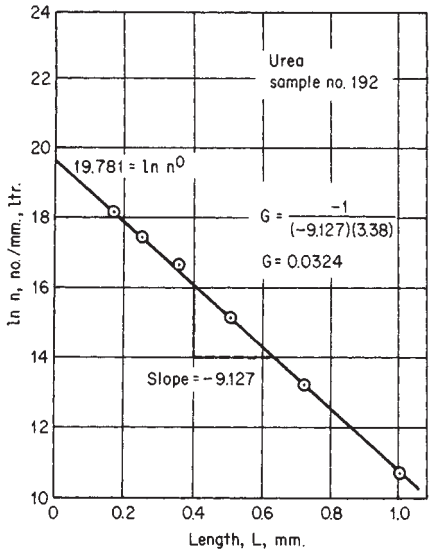


FIG. 18-61 Population density plot for Example 3.

crystallizer, is by far the most important in use today. In most commercial equipment of this type, the uniformity of suspension of product solids within the crystallizer body is sufficient for the theory [Eqs. (18-31) to (18-33*b*)] to apply. Although a number of different varieties and features are included within this classification, the equipment operating with the highest capacity is the kind in which the vaporization of a solvent, usually water, occurs.

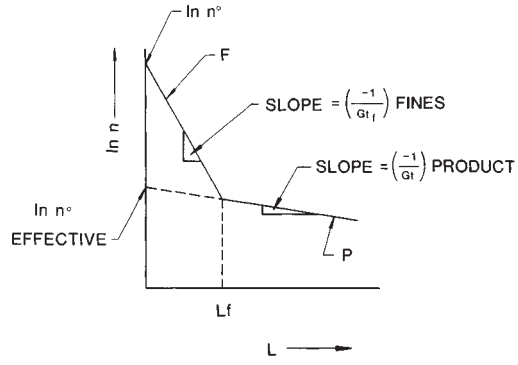


FIG. 18-62 Plot of Log *N* against *L* for a crystallizer with fines removal.

Although surface-cooled types of MSMPR crystallizers are available, most users prefer crystallizers employing vaporization of solvents or of refrigerants. The primary reason for this preference is that heat transferred through the critical supersaturating step is through a boiling-liquid-gas surface, avoiding the troublesome solid deposits that can form on a metal heat-transfer surface.

Forced-Circulation Evaporator-Crystallizer This crystallizer is shown in Fig. 18-64. Slurry leaving the body is pumped through a circulating pipe and through a tube-and-shell heat exchanger, where its temperature increases by about 2 to 6°C (3 to 10°F). Since this heating is done without vaporization, materials of normal solubility should produce no deposition on the tubes. The heated slurry, returned to the body by a recirculation line, mixes with the body slurry and raises its temperature locally near the point of entry, which causes boiling at the liquid surface. During the consequent cooling and

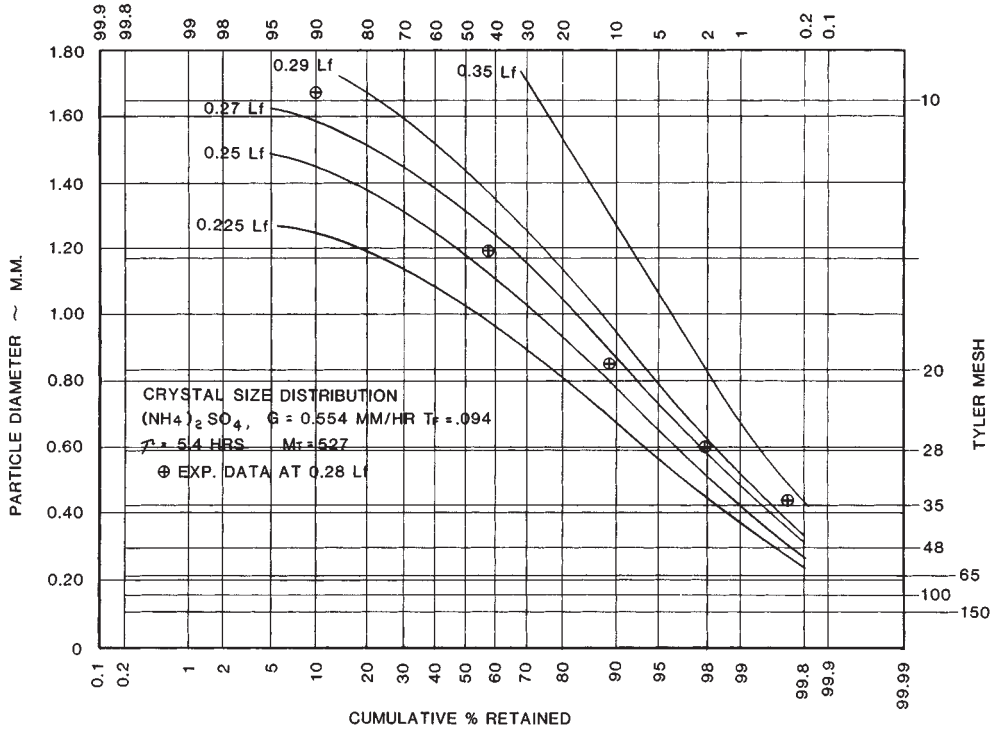


FIG. 18-63 Calculated product-size distribution for a crystallizer operation at different fine-crystal-separation sizes.

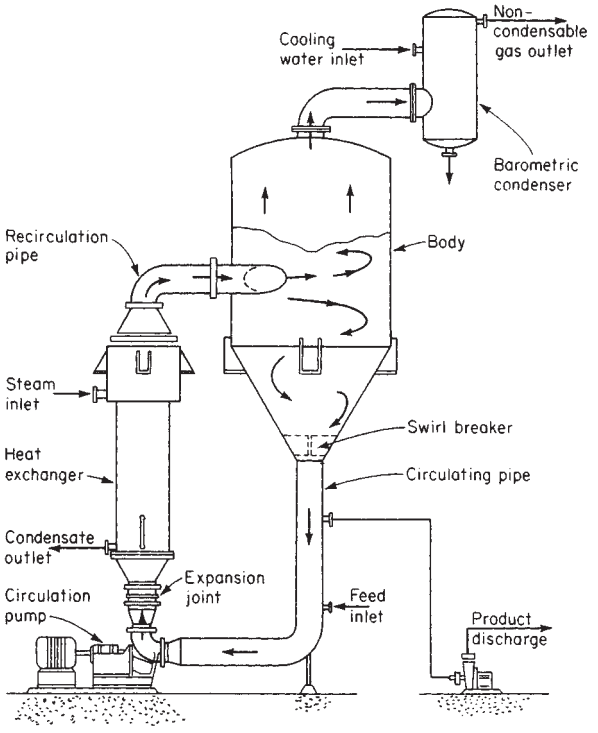


FIG. 18-64 Forced-circulation (evaporative) crystallizer. (*Swenson Process Equipment, Inc.*)

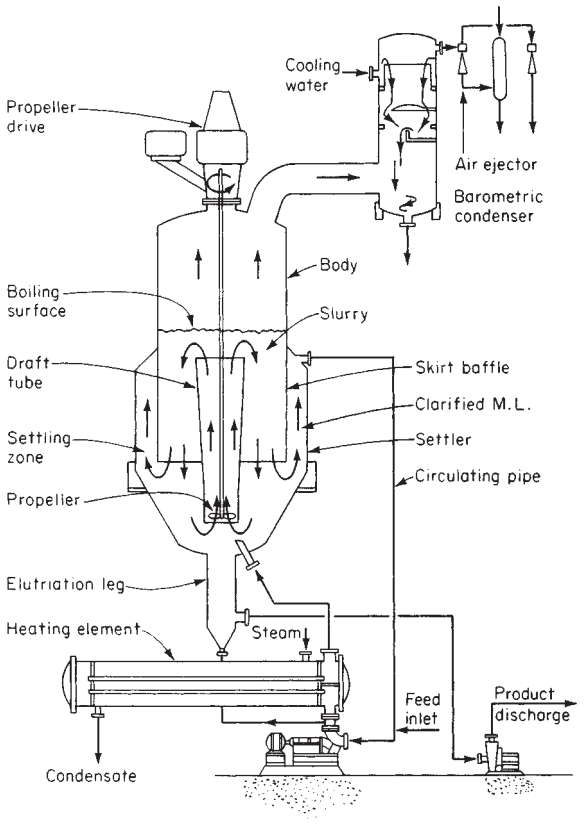


FIG. 18-65 Draft-tube-baffle (DTB) crystallizer. (*Swenson Process Equipment, Inc.*)

vaporization to achieve equilibrium between liquid and vapor, the supersaturation which is created causes deposits on the swirling body of suspended crystals until they again leave via the circulating pipe. The quantity and the velocity of the recirculation, the size of the body, and the type and speed of the circulating pump are critical design items if predictable results are to be achieved. A further discussion of the parameters affecting this type of equipment is given by Bennett, Newman, and Van Buren [*Chem. Eng. Prog.*, **55**(3), 65 (1959); *Chem. Eng. Prog. Symp. Ser.*, **65**(95), 34, 44 (1969)].

If the crystallizer is not of the evaporative type but relies only on *adiabatic evaporative cooling* to achieve the yield, the heating element is omitted. The feed is admitted into the circulating line after withdrawal of the slurry, at a point sufficiently below the free-liquid surface to prevent flashing during the mixing process.

Draft-Tube-Baffle (DTB) Evaporator-Crystallizer Because mechanical circulation greatly influences the level of nucleation within the crystallizer, a number of designs have been developed that use circulators located within the body of the crystallizer, thereby reducing the head against which the circulator must pump. This technique reduces the power input and circulator tip speed and therefore the rate of nucleation. A typical example is the draft-tube-baffle (DTB) evaporator-crystallizer (Swenson Process Equipment, Inc.) shown in Fig. 18-65. The suspension of product crystals in maintained by a large, slow-moving propeller surrounded by a draft tube within the body. The propeller directs the slurry to the liquid surface so as to prevent solids from short-circuiting the zone of the most intense supersaturation. Slurry which has been cooled is returned to the bottom of the vessel and recirculated through the propeller. At the propeller, heated solution is mixed with the recirculating slurry.

The design of Fig. 18-65 contains a fines-destruction feature comprising the settling zone surrounding the crystallizer body, the circulating pump, and the heating element. The heating element supplies sufficient heat to meet the evaporation requirements and to raise the temperature of the solution removed from the settler so as to destroy any small crystalline particles withdrawn. Coarse crystals are separated from the fines in the settling zone by gravitational sedimentation, and therefore this fines-destruction feature is applicable only to systems in which there is a substantial density difference between crystals and mother liquor.

This type of equipment can also be used for applications in which the only heat removed is that required for adiabatic cooling of the incoming feed solution. When this is done and the fines-destruction feature is to be employed, a stream of liquid must be withdrawn from the settling zone of the crystallizer and the fine crystals must be separated or destroyed by some means other than heat addition—for example, either dilution or thickening and physical separation.

In some crystallization applications it is desirable to increase the solids content of the slurry within the body above the natural consistency, which is that developed by equilibrium cooling of the incoming feed solution to the final temperature. This can be done by withdrawing a stream of mother liquor from the baffle zone, thereby thickening the slurry within the growing zone of the crystallizer. This mother liquor is also available for removal of fine crystals for size control of the product.

Draft-Tube (DT) Crystallizer This crystallizer may be employed in systems in which fines destruction is not needed or wanted. In such cases the baffle is omitted, and the internal circulator is sized to have the minimum nucleating influence on the suspension.

In DTB and DT crystallizers the circulation rate achieved is generally much greater than that available in a similar forced-circulation crystallizer. The equipment therefore finds application when it is necessary to circulate large quantities of slurry to minimize supersaturation levels within the equipment. In general, this approach is required to obtain long operating cycles with material capable of growing on

the walls of the crystallizer. The draft-tube and draft-tube-baffle designs are commonly used in the production of granular materials such as ammonium sulfate, potassium chloride, photographic hypo, and other inorganic and organic crystals for which product in the range 8 to 30 mesh is required.

Surface-Cooled Crystallizer For some materials, such as sodium chlorate, it is possible to use a forced-circulation tube-and-shell exchanger in direct combination with a draft-tube-crystallizer body, as shown in Fig. 18-66. Careful attention must be paid to the temperature difference between the cooling medium and the slurry circulated through the exchanger tubes. In addition, the path and rate of slurry flow within the crystallizer body must be such that the volume contained in the body is "active." That is to say, crystals must be so suspended within the body by the turbulence that they are effective in relieving supersaturation created by the reduction in temperature of the slurry as it passes through the exchanger. Obviously, the circulating pump is part of the crystallizing system, and careful attention must be paid to its type and its operating parameters to avoid undue nucleating influences.

The use of the internal baffle permits operation of the crystallizer at a slurry consistency other than that naturally obtained by the cooling of the feed from the initial temperature to the final mother-liquor temperature. The baffle also permits fines removal and destruction.

With most inorganic materials this type of equipment produces crystals in the range 30 to 100 mesh. The design is based on the allowable rates of heat exchange and the retention required to grow the product crystals.

Direct-Contact-Refrigeration Crystallizer For some applications, such as the freezing of ice from seawater, it is necessary to go to such low temperatures that cooling by the use of refrigerants is the only economical solution. In such systems it is sometimes impractical to employ surface-cooled equipment because the allowable temperature difference is so small (under 3°C) that the heat-exchanger surface becomes excessive or because the viscosity is so high that the mechanical energy put in by the circulation system requires a heat-removal rate greater than can be obtained at reasonable temperature differences. In such systems, it is convenient to admix the refrigerant with the slurry being cooled in the crystallizer, as shown in Fig. 18-67, so that the heat of vaporization of the refrigerant cools the slurry by direct contact. The successful application of such systems requires that the refrigerant be relatively immiscible with the mother liquor and be capable of separation, compression, condensation, and subsequent recycle into the crystallizing system. The operating pressures and temperatures chosen have a large bearing on power consumption.

This technique has been very successful in reducing the problems associated with buildup of solids on a cooling surface. The use of direct-contact refrigeration also reduces overall process-energy requirements, since in a refrigeration process involving two fluids a greater temperature difference is required on an overall basis when the refrigerant must first cool some intermediate solution, such as calcium chloride brine, and that solution in turn cools the mother liquor in the crystallizer.

Equipment of this type has been successfully operated at temperatures as low as –59°C (–75°F).

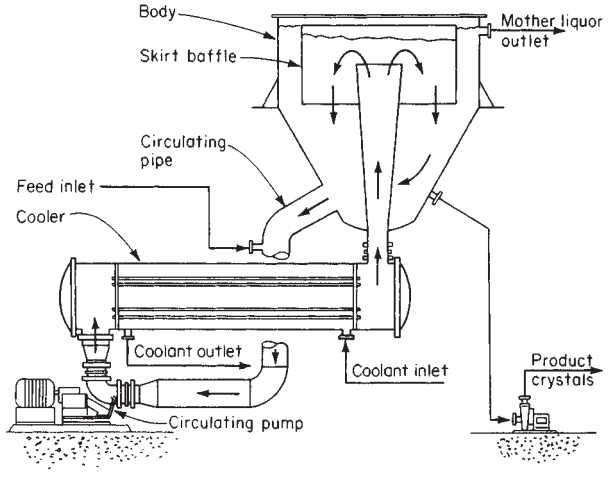


FIG. 18-66 Forced-circulation baffle surface-cooled crystallizer. (*Swenson Process Equipment, Inc.*)

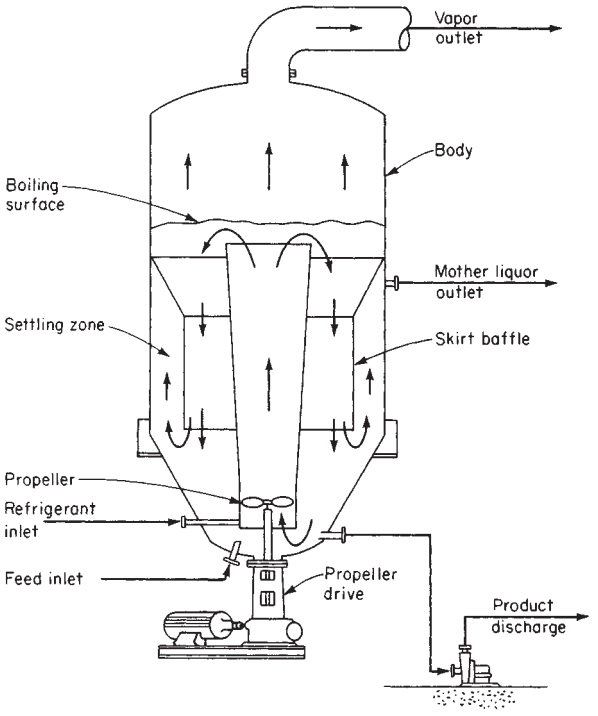


FIG. 18-67 Direct-contact-refrigeration crystallizer (DTB type). (*Swenson Process Equipment, Inc.*)

Reaction-Type Crystallizers In chemical reactions in which the end product is a solid-phase material such as a crystal or an amorphous solid the type of equipment described in the preceding subsections or shown in Fig. 18-68 may be used. By mixing the reactants in a large circulated stream of mother liquor containing suspended solids of the equilibrium phase, it is possible to minimize the driving force created during their reaction and remove the heat of reaction through the vaporization of a solvent, normally water. Depending on the final particle size required, it is possible to incorporate a fines-destruction baffle as shown in Fig. 18-68 and take advantage of the control over particle size afforded by this technique. In the case of ammonium sulfate crystallization from ammonia gas and concentrated sulfuric acid, it is necessary to vaporize water to remove the heat of reaction, and this water so removed can be reinjected after condensation into the fines-destruction stream to afford a very large amount of dissolving capability.

Other examples of this technique are where a solid material is to be decomposed by mixing it with a mother liquor of a different composition, as shown in Fig. 18-69. Carnallite ore ($KCl{\cdot}MgCl_2{\cdot}4H_2O$) can be added to a mother liquor into which water is also added so that decomposition of the ore into potassium chloride (KCl) crystals and magnesium chloride–rich mother liquor takes place. Circulated slurry in the draft tube suspends the product crystals as well as the incoming ore particles until the ore can decompose into potassium chloride crystals and mother liquor. By taking advantage of the fact that water must be added to the process, the fines-bearing mother liquor can be removed behind the baffle and then water added so that the finest particles are dissolved before being returned to the crystallizer body.

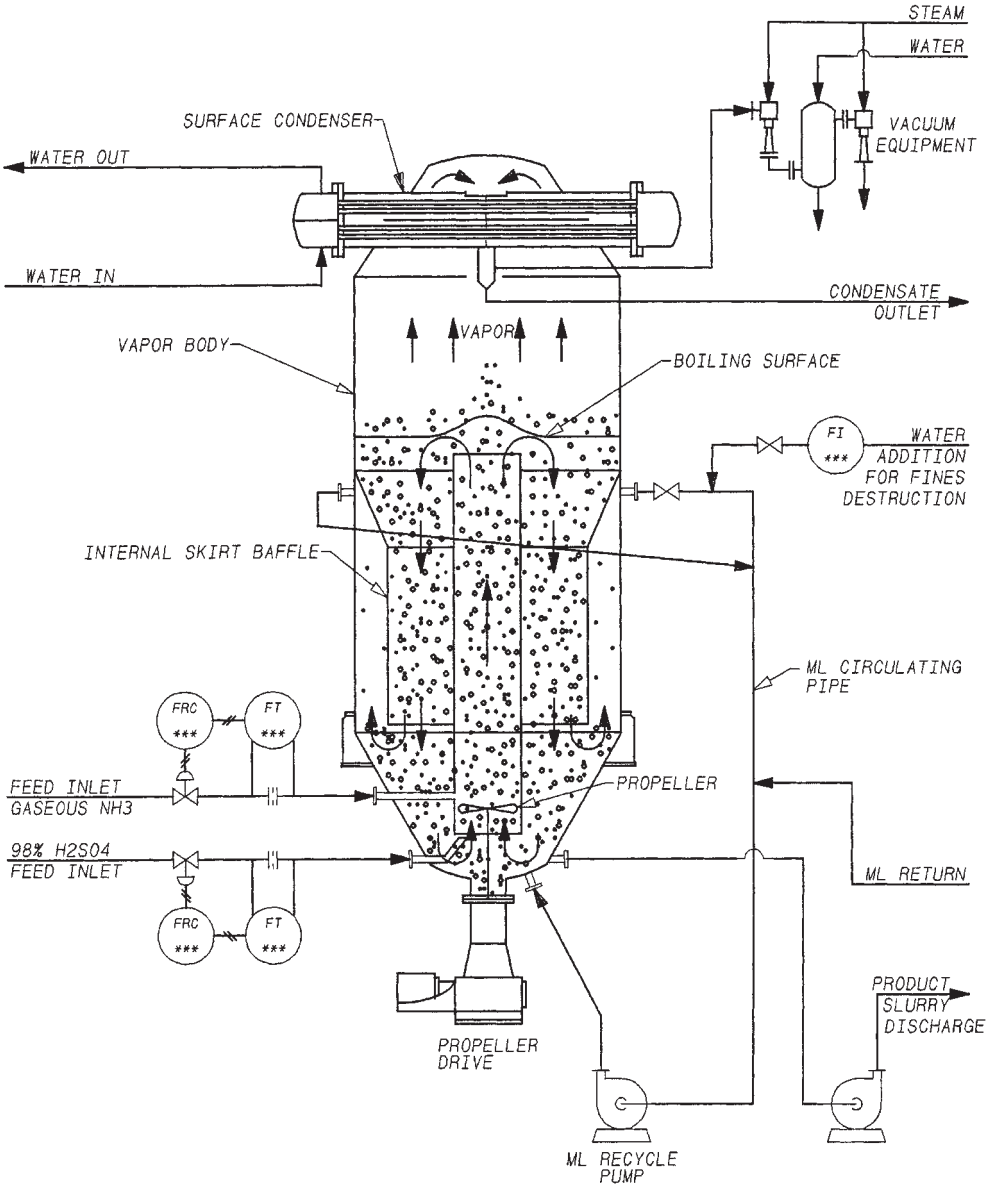


FIG. 18-68 Swenson reaction type DTB crystallizer. (*Swenson Process Equipment, Inc.*)

Other examples of this technique involve neutralization reactions such as the neutralization of sulfuric acid with calcium chloride to result in the precipitation of gypsum.

Mixed-Suspension, Classified-Product-Removal Crystallizers Many of the crystallizers just described can be designed for classified-product discharge. Classification of the product is normally done by means of an elutriation leg suspended beneath the crystallizing body as shown in Fig. 18-66. Introduction of clarified mother liquor to the lower portion of the leg fluidizes the particles prior to discharge and selectively returns the finest crystals to the body for further growth. A relatively wide distribution of material is usually produced unless the elutriation leg is extremely long. Inlet conditions at the leg are critical if good classifying action or washing action is to be achieved.

If an elutriation leg or other product-classifying device is added to a crystallizer of the MSMPR type, the plot of the population density versus L is distorted in the region of largest sizes. Also the incorporation of an elutriation leg destabilizes the crystal-size distribution and under some conditions can lead to cycling. The theoretical treatment of both the crystallizer model and the cycling relations is discussed by Randolph, Beer, and Keener (loc. cit.). Although such a feature can be included on many types of classified-suspension or mixed-suspension crystallizers, it is most common to use this feature with the forced-circulation evaporative-crystallizer and the DTB crystallizer.

Classified-Suspension Crystallizer This equipment is also known as the **growth** or **Oslo crystallizer** and is characterized by the production of supersaturation in a circulating stream of liquor. Supersaturation is developed in one part of the system by evaporative cooling or by cooling in a heat exchanger, and it is relieved by passing the liquor through a fluidized bed of crystals. The fluidized bed may be contained in a simple tank or in a more sophisticated vessel arranged

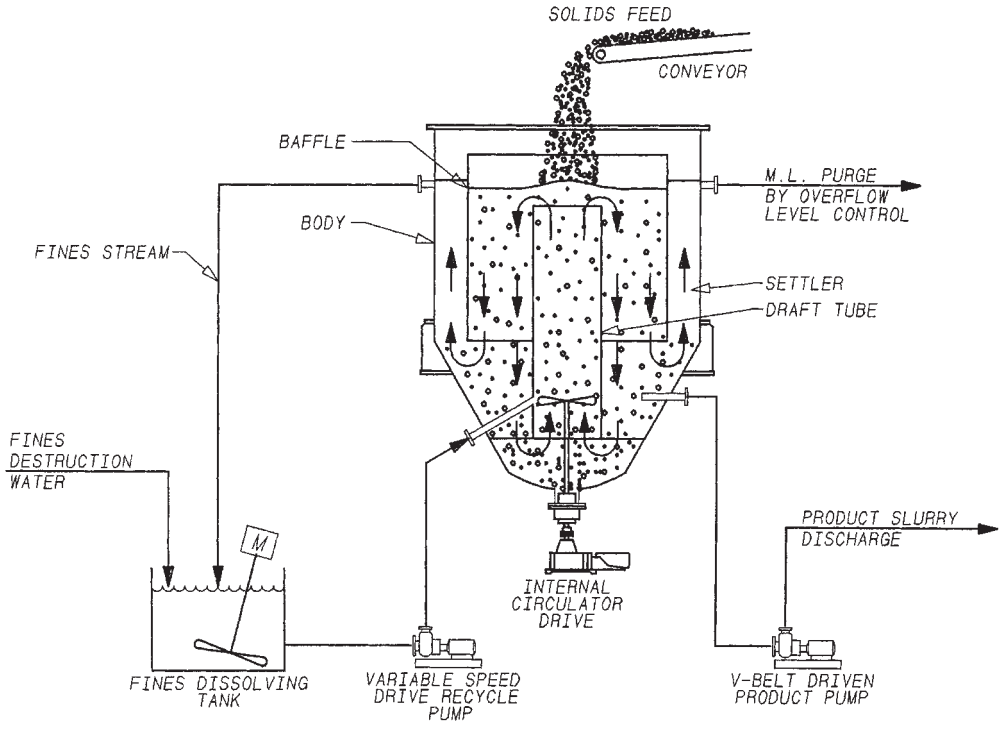


FIG. 18-69 Swenson atmospheric reaction–type DTB crystallizer. (*Swenson Process Equipment, Inc.*)

for a pronounced classification of the crystal sizes. Ideally this equipment operates within the metastable supersaturation field described by Miers and Isaac, *J. Chem. Soc.*, **1906,** 413.

In the **evaporative crystallizer** of Fig. 18-70, solution leaving the vaporization chamber at *B* is supersaturated slightly within the metastable zone so that new nuclei will not form. The liquor contacting the bed at *E* relieves its supersaturation on the growing crystals and leaves through the circulating pipe *F.* In a cooling-type crystallization hot feed is introduced at *G,* and the mixed liquor flashes when it reaches the vaporization chamber at *A.* If further evaporation is required to produce the driving force, a heat exchanger is installed between the circulating pump and the vaporization changer to supply the heat for the required rate of vaporization.

The transfer of supersaturated liquor from the vaporizer (point *B,* Fig. 18-69) often causes salt buildup in the piping and reduction of the operating cycle in equipment of this type. The rate of buildup can be reduced by circulating a thin suspension of solids through the vaporizing chamber; however, the presence of such small seed crystals tends to rob the supersaturation developed in the vaporizer, thereby lowering the efficiency of the recirculation system.

An **Oslo surface-cooled crystallizer** is illustrated in Fig. 18-71. Supersaturation is developed in the circulated liquor by chilling in the cooler *H.* This supersaturated liquor is contacted with the suspension of crystals in the suspension chamber at *E.* At the top of the suspension chamber a stream of mother liquor *D* can be removed to be used for fines removal and destruction. This feature can be added on either type of equipment. Fine crystals withdrawn from the top of the suspension are destroyed, thereby reducing the overall number of crystals in the system and increasing the particle size of the remaining product crystals.

Scraped-Surface Crystallizer For relatively small-scale applications a number of crystallizer designs employing direct heat exchange between the slurry and a jacket or double wall containing a cooling medium have been developed. The heat-transfer surface is scraped or agitated in such a way that the deposits cannot build up. The scraped-surface crystallizer provides an effective and inexpensive method of producing slurry in equipment which does not require expensive installation or supporting structures.

Double-Pipe Scraped-Surface Crystallizer This type of equipment consists of a double-pipe heat exchanger with an internal agitator fitted with spring-loaded scrapers that wipe the wall of the inner pipe. The cooling liquid passes between the pipes, this annulus being dimensioned to permit reasonable shell-side velocities. The scrapers prevent the buildup of solids and maintain a good film coefficient of heat transfer. The equipment can be operated in a continuous or in a recirculating batch manner.

Such units are generally built in lengths to above 12 m (40 ft). They can be arranged in parallel or in series to give the necessary liquid velocities for various capacities. Heat-transfer coefficients have been reported in the range of 170 to 850 W/(m^2·K) [30 to 150 Btu/(h·ft^2·°F)] at temperature differentials of 17°C (30°F) and higher [Garrett and Rosenbaum, *Chem. Eng.*, **65**(16), 127 (1958)]. Equipment of this type is marketed as the **Votator** and the **Armstrong crystallizer.**

Batch Crystallization Batch crystallization has been practiced longer than any other form of crystallization in both atmospheric tanks, which are either static or agitated, as well as in vacuum or pressure vessels. It is still widely practiced in the pharmaceutical and fine chemical industry or in those applications where the capacity is very small. The integrity of the batch with respect to composition and history can be maintained easily and the inventory management is more precise than with continuous processes. Batch crystallizers can be left unattended (overnight) if necessary and this is an important advantage for many small producers.

In any batch process the common mode of operation involves charging the crystallizer with concentrated or near-saturated solution, producing supersaturation by means of cooling the batch or evaporating solvent from the batch, seeding the batch by means of injecting seed crystals into the batch or by allowing homogeneous nucleation to occur, reaching the final mother-liquor temperature and concentration by some time-dependent means of control, and stopping the cycle

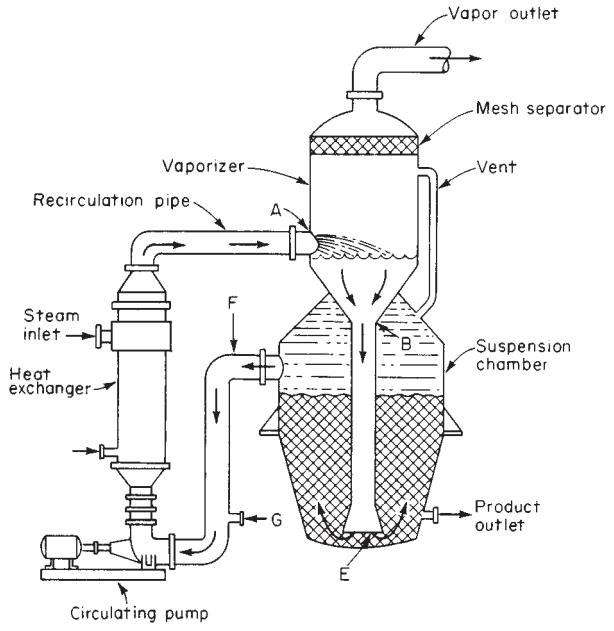


FIG. 18-70 OSLO evaporative crystallizer.

so that the batch may be dumped into a tank for processing by successive steps, which normally include centrifugation, filtration, and/or drying. In some cases, a small "heal" of slurry is left in the batch crystallizer to act as seed for the next batch.

Control of a batch crystallizer is almost always the most difficult part and very often is not practiced except to permit homogeneous nucleation to take place when the system becomes supersaturated. If control is practiced, it is necessary to have some means for determining when the initial solution is supersaturated so that seed of the appropriate size, quantity, and habit may be introduced into the batch. Following seeding, it is necessary to limit the cooling or evaporation in the batch to that which permits the generated supersaturation to be relieved on the seed crystals. This means that the first cooling or evaporation following seeding must be at a very slow rate, which is increased nonlinearly in order to achieve the optimum batch cycle. Frequently, such controls are operated by cycle timers or computers so as to achieve the required conditions. Sugar, many pharmaceutical products, and many fine chemicals are produced this way. Shown in Fig. 18-72 is a typical batch crystallizer comprising a jacketed closed tank with top-mounted agitator and feed connections. The tank is equipped with a short distillation column and surface condenser so that volatile materials may be retained in the tank and solvent recycled to maintain the batch integrity. Provisions are included so that the vessel may be heated with steam addition to the shell or cooling solution circulated through the jacket so as to control the temperature. Tanks of this type are intended to be operated with a wide variety of chemicals under both cooling and solvent evaporation conditions.

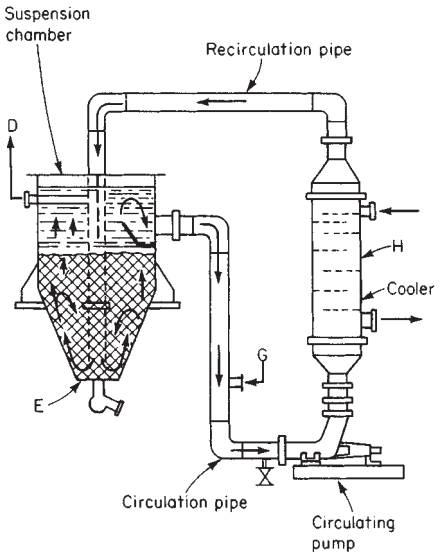


FIG. 18-71 OSLO surface-cooled crystallizer.

Recompression Evaporation-Crystallization In all types of crystallization equipment wherein water or some other solvent is vaporized to produce supersaturation and/or cooling, attention should be given to the use of mechanical vapor recompression, which by its nature permits substitution of electrical energy for evaporation and solvent removal rather than requiring the direct utilization of heat energy in the form of steam or electricity. A typical recompression crystallizer flowsheet is shown in Fig. 18-73, which shows a single-stage evaporative crystallizer operating at approximately atmospheric pressure. The amount of heat energy necessary to remove 1 kg of water to produce the equivalent in crystal product is approximately 550 kilocalories. If the water evaporated is compressed by a mechanical compressor of high efficiency to a pressure where it can be condensed in the heat exchanger of the crystallizer, it can thereby supply the energy needed to sustain the process. Then the equivalent power for this compression is about 44 kilocalories (Bennett, *Chem. Eng. Progress,* 1978, pp. 67–70).

Although this technique is limited economically to those large-scale cases where the materials handled have a relatively low boiling point elevation and in those cases where a significant amount of heat is required to produce the evaporation for the crystallization step, it nevertheless offers an attractive technique for reducing the use of heat energy and substituting mechanical energy or electrical energy in those cases where there is a cost advantage for doing so. This technique finds many applications in the crystallization of sodium sulfate, sodium carbonate monohydrate, and sodium chloride. Shown in Fig. 18-74 is the amount of vapor compressed per kilowatt-hour for water vapor at 100°C and various ΔTs. The amount of water vapor compressed per horsepower decreases rapidly with increasing ΔT and, therefore, normal design considerations dictate that the recompression evaporators have a relatively large amount of heat-transfer surface so as to minimize the power cost. Often this technique is utilized only with the initial stages of evaporation where concentration of the solids is relatively low and, therefore, the boiling-point elevation is negligible. In order to maintain adequate tube velocity for heat transfer and suspension of crystals, the increased surface requires a large internal recirculation within the crystallizer body, which consequently lowers the supersaturation in the fluid pumped through the tubes. One benefit of this design is that with materials of flat or inverted solubility, the use of recompression complements the need to maintain low ΔTs to prevent fouling of the heat-transfer surface.

INFORMATION REQUIRED TO SPECIFY A CRYSTALLIZER

The following information regarding the product, properties of the feed solution, and required materials of construction must be available before a crystallizer application can be properly evaluated and the appropriate equipment options identified. Is the crystalline material being produced a hydrated or an anhydrous material? What is the solubility of the compound in water or in other solvents under consideration, and how does this change with temperature? Are other compounds in solution which coprecipitate with the product being crystallized, or do these remain in solution, increasing in concentration until some change in product phase occurs? What will be the influence of impurities in the solution on the crystal habit, growth, and

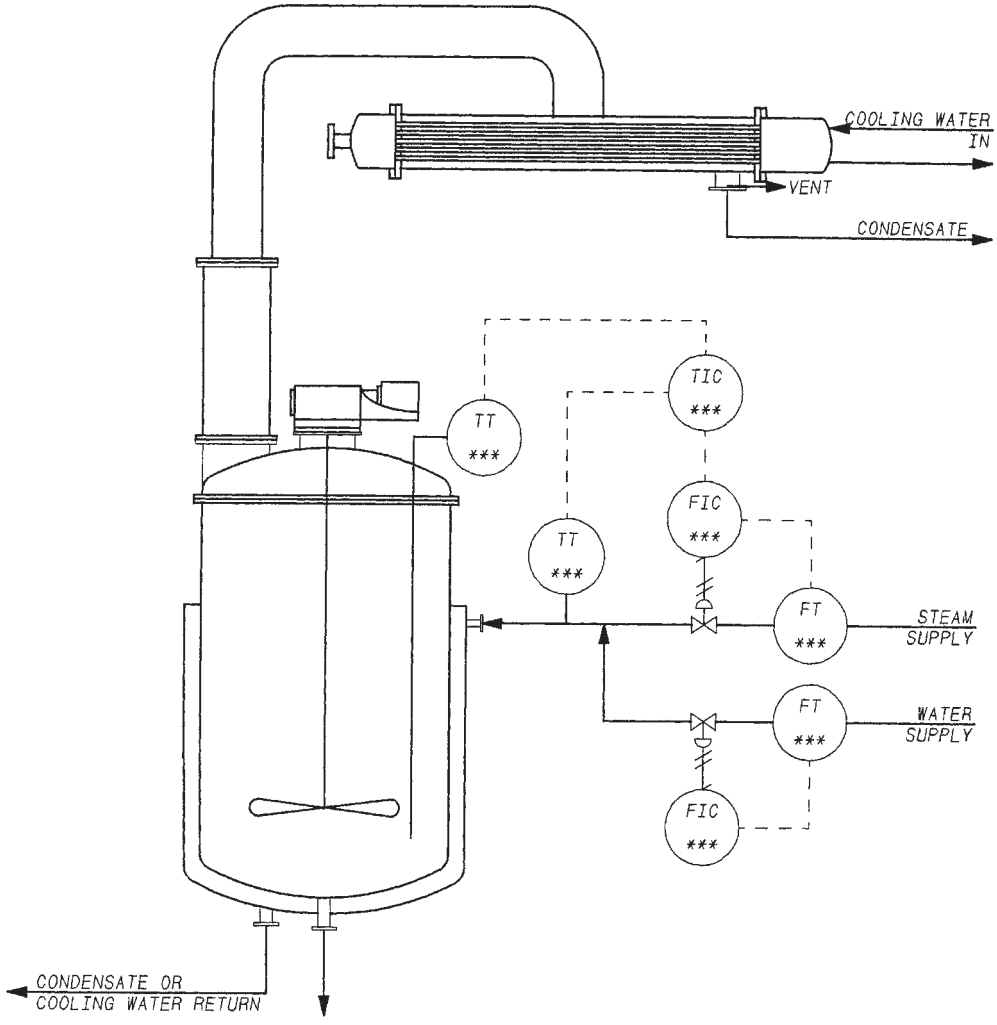


FIG. 18-72 Typical agitated batch crystallizer. (*Swenson Process Equipment, Inc.*)

nucleation rates? What are the physical properties of the solution and its tendency to foam? What is the heat of crystallization of the product crystal? What is the production rate, and what is the basis on which this production rate is computed? What is the tendency of the material to grow on the walls of the crystallizer? What materials of construction can be used in contact with the solution at various temperatures? What utilities will be available at the crystallizer location, and what are the costs associated with the use of these utilities? Is the final product to be blended or mixed with other crystalline materials or solids? What size of product and what shape of product are required to meet these requirements? How can the crystalline material be separated from the mother liquor and dried? Are there temperature requirements or wash requirements which must be met? How can these solids or mixtures of solids be handled and stored without undue breakage and caking?

Another basic consideration is whether crystallization is best carried out on a batch basis or on a continuous basis. The present tendency in most processing plants is to use continuous equipment whenever possible. Continuous equipment permits adjusting of the operating variables to a relatively fine degree in order to achieve the best results in terms of energy usage and product characteristics. It allows the use of a smaller labor force and results in a continuous utility demand, which minimizes the size of boilers, cooling towers, and power-generation facilities. It also minimizes the capital investment required in the crystallizer and in the feed-storage and product-liquor-storage facilities.

Materials that have a tendency to grow readily on the walls of the crytallizer require periodic washout, and therefore an otherwise continuous operation would be interrupted once or even twice a week for the removal of these deposits. The impact that this contingency may have on the processing-equipment train ahead of the crystallizer must be considered.

The batch handling of wet or semidry crystalline materials is substantially more difficult than the storing and handling of dry crystalline materials. A batch operation has economic application only on a relatively small scale or when temperature or product characteristics require unusual precautions.

CRYSTALLIZER OPERATION

Crystal growth is a layer-by-layer process, and the retention time required in most commercial equipment to produce crystals of the size normally desired is on the order of 2 to 6 h. On the other hand, nucleation in a supersaturated solution can be generated in a fraction

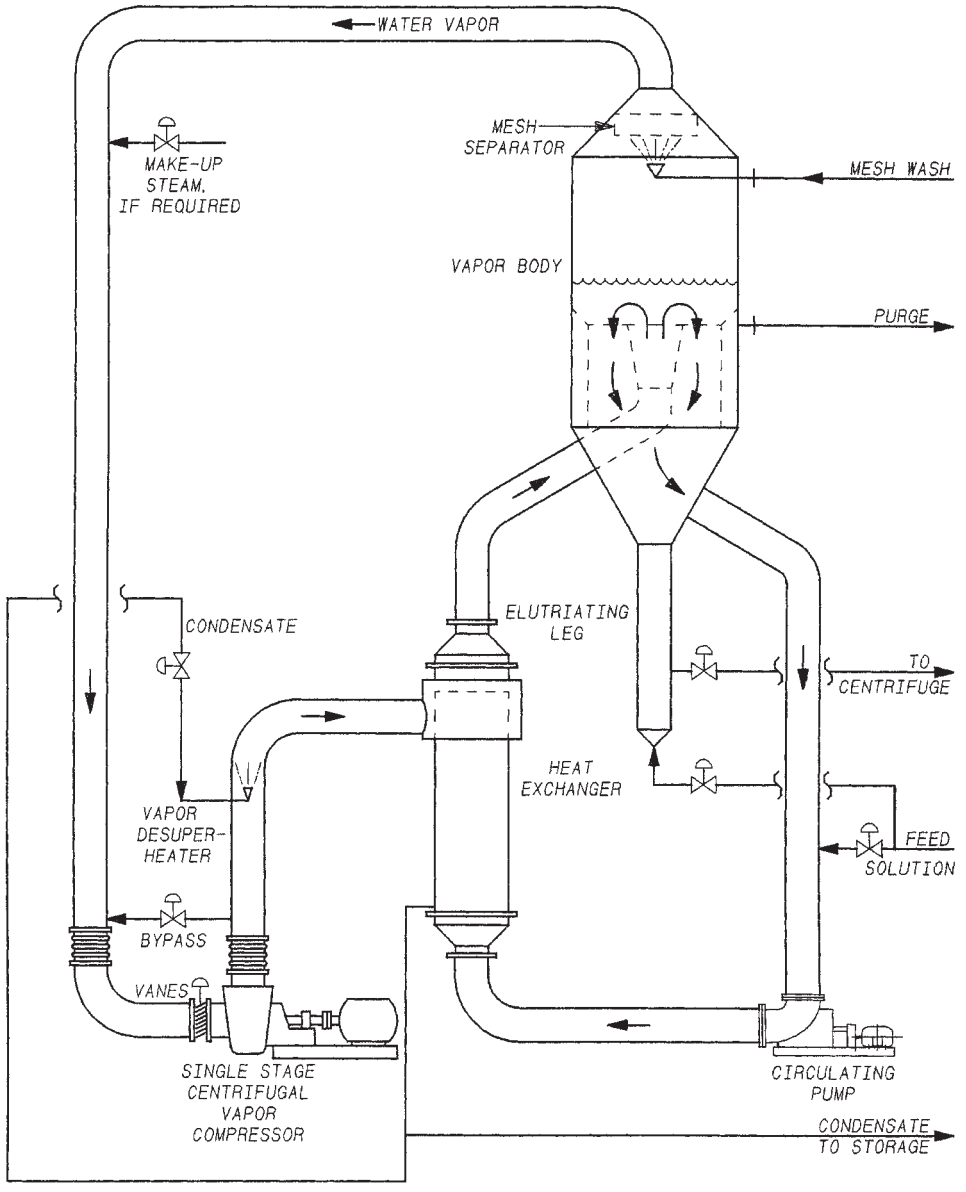


FIG. 18-73 Swenson single-stage recompression evaporator. (*Swenson Process Equipment, Inc.*)

of a second. The influence of any upsets in operating conditions, in terms of the excess nuclei produced, is very short-term in comparison with the total growth period of the product removed from the crystallizer. In a practical sense, this means that steadiness of operation is much more important in crystallization equipment than it is in many other types of process equipment.

It is to be expected that four to six retention periods will pass before the effects of an upset will be damped out. Thus, the recovery period may last from 8 to 36 h.

The **rate of nuclei formation** required to sustain a given product size decreases exponentially with increasing size of the product. Although when crystals in the range of 100 to 50 mesh are produced, the system may react quickly, the system response when generating large crystals in the 14-mesh size range is quite slow. This is because a single pound of 150-mesh seed crystals is sufficient to provide the total number of particles in a ton of 14-mesh product crystals. In any system producing relatively large crystals, nucleation must be carefully controlled with respect to all internal and external sources. Particular attention must be paid to preventing seed crystals from entering with the incoming feed stream or being returned to the crystallizer with recycle streams of mother liquor coming back from the filter or centrifuge.

Experience has shown that in any given body operating at a given production rate, control of the magma (slurry) density is important to the control of crystal size. Although in some systems a change in slurry density does not result in a change in the rate nucleation, the more general case is that an increase in the magma density increases the product size through reduction in nucleation and increased retention time of the crystals in the growing bed. The reduction in supersaturation at longer retention times together with the smaller distance

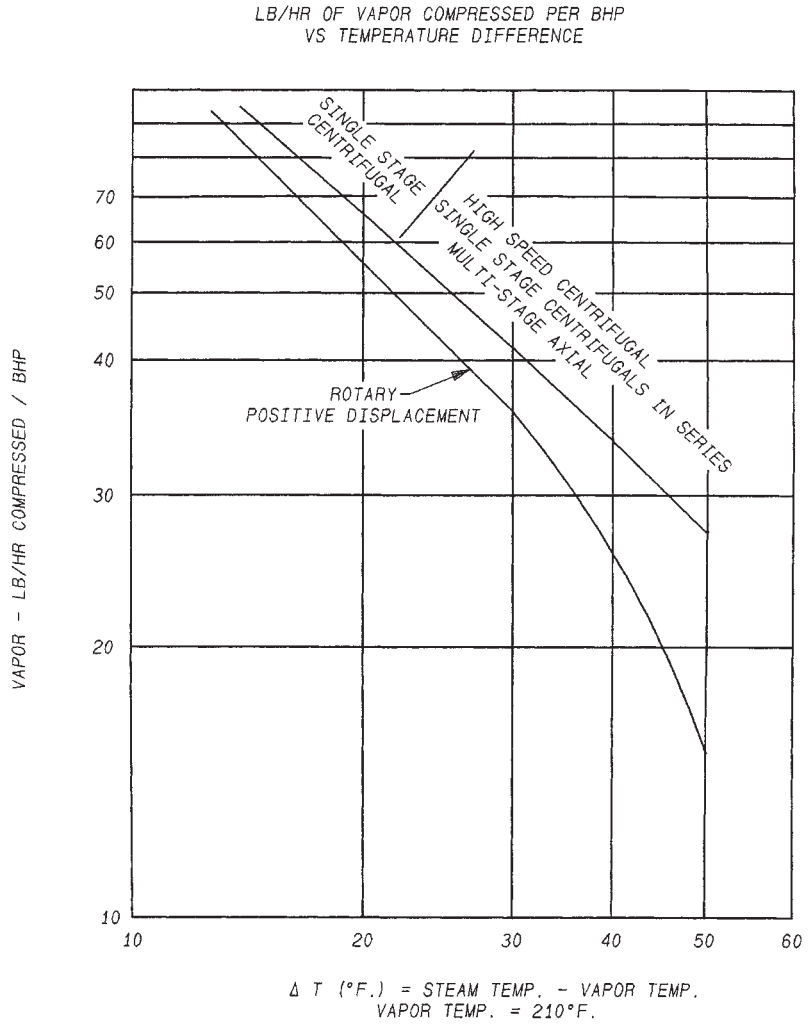


FIG. 18-74 Recompression evaporator horsepower as a function of overall ΔT.

between growing crystals, which lowers the driving force that is required to transport material from the liquid phase to the growing solids (**propinquity effect**), appears to be responsible for the larger product.

A reduction in the magma density will generally increase nucleation and decrease the particle size. This technique has the disadvantage that crystal formation on the equipment surfaces increases because lower slurry densities create higher levels of supersaturation within the equipment, particularly at the critical boiling surface in a vaporization-type crystallizer.

High levels of supersaturation at the liquid surface or at the tube walls in a surface-cooled crystallizer are the dominant cause of wall salting. Although some types of crystallizers can operate for several months continuously when crystallizing KCl or $(NH_4)_2SO_4$, most machines have much shorter operating cycles. Second only to control of particle size, the extension of operating cycles is the most difficult operating problem to be solved in most installations.

In the forced-circulation-type crystallizer (Fig. 19-43) primary control over particle size is exercised by the designer in selecting the circulating system and volume of the body. From the operating standpoint there is little that can be done to an existing unit other than supply external seed, classify the discharge crystals, or control the slurry density. Nevertheless, machines of this type are frequently carefully controlled by these techniques and produce a predictable and desirable product-size distribution.

When crystals cannot be grown sufficiently large in forced-circulation equipment to meet product-size requirements, it is common to employ one of the designs that allow some influence to be exercised over the population density of the finer crystals. In the DTB design (Fig. 18-69) this is done by regulating the flow in the circulating pipe so as to withdraw a portion of the fines in the body in the amount of about 0.05 to 0.5 percent by settled volume. The exact quantity of solids depends on the size of the product crystals and on the capacity of the fines-dissolving system. If the machine is not operating stably, this quantity of solids will appear and then disappear, indicating changes in the nucleation rate within the circuit. At steady-state operation, the quantity of solids overflowing will remain relatively constant, with some solids appearing at all times. Should the slurry density of product crystals circulated within the machine rise to a value higher than about 50 percent settled volume, large quantities of product crystals will appear in the overflow system, disabling the fines-destruction equipment. Too high a circulating rate through the fines trap will produce this same result. Too low a flow through the fines circuit will remove insufficient particles and result in a

smaller product-size crystal. To operate effectively, a crystallizer of the type employing fines-destruction techniques requires more sophisticated control than does operation of the simpler forced-circulation equipment.

The classifying crystallizer (Fig. 18-70) requires approximately the same control of the fines-removal stream and, in addition, requires control of the fluidizing flow circulated by the main pump. This flow must be adjusted to achieve the proper degree of fluidization in the suspension chamber, and this quantity of flow varies as the crystal size varies between start-up operation and normal operation. As with the draft-tube-baffle machine, a considerably higher degree of skill is required for operation of this equipment than of the forced-circulation type.

While most of the industrial designs in use today are built to reduce the problems due to excess nucleation, it is true that in some crystallizing systems a deficiency of seed crystals is produced and the product crystals are larger than are wanted or required. In such systems nucleation can be increased by increasing the mechanical stimulus created by the circulating devices or by seeding through the addition of fine crystals from some external source.

CRYSTALLIZER COSTS

Because crystallizers can come with such a wide variety of attachments, capacities, materials of construction, and designs, it is very difficult to present an accurate picture of the costs for any except certain specific types of equipment, crystallizing specific compounds. This is illustrated in Fig. 18-75, which shows the prices of equipment for crystallizing two different compounds at various production rates, one of the compounds being produced in two alternative crystallizer modes. Installed cost (including cost of equipment and accessories, foundations and supporting steel, utility piping,

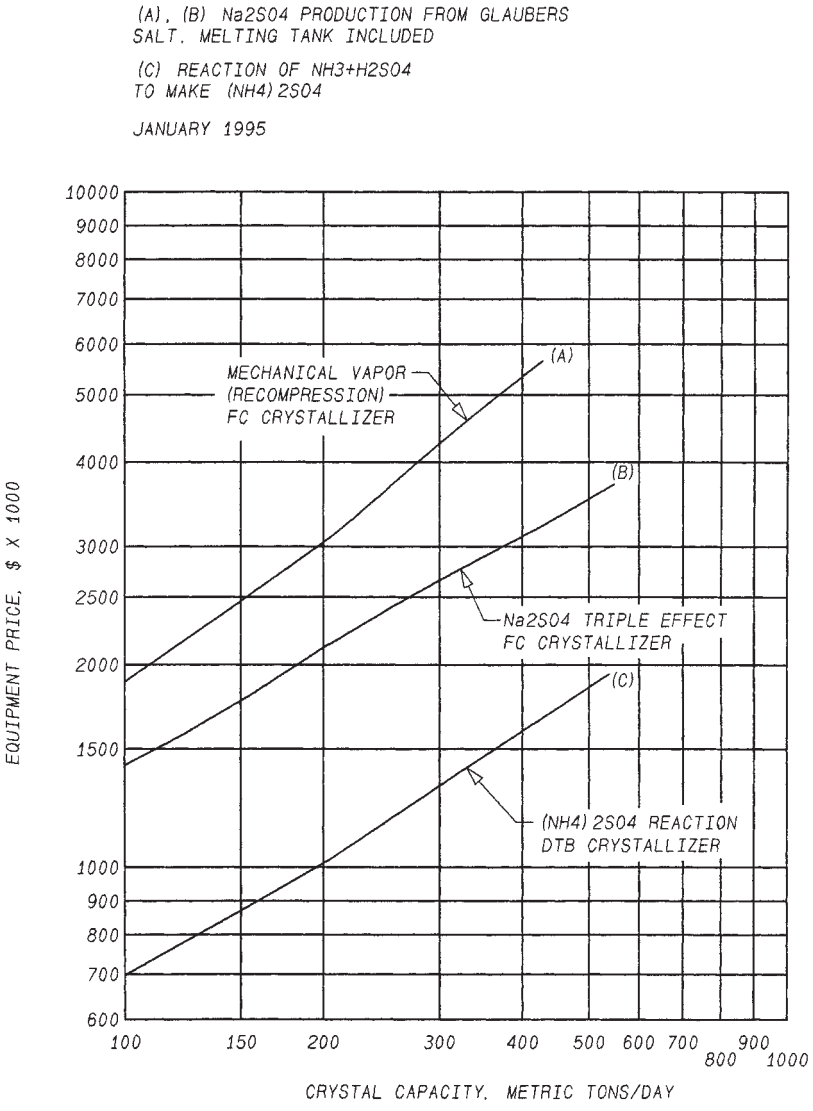


FIG. 18-75 Equipment prices, FOB point of fabrication, for typical crystallizer systems. Prices are for crystallizer plus accessories including vacuum equipment. (*Data supplied by Swenson Process Equipment, Inc., effective January, 1995.*)

process piping and pumps, electrical switchgear, instrumentation, and labor, but excluding cost of a building) will be approximately twice these price figures.

It should be ever present in the reader's mind that for every particular case the appropriate crystallizer manufacturers should be consulted for reliable price estimates. Most crystallization equipment is custom-designed, and costs for a particular application may vary greatly from those illustrated in Fig. 18-75. Realistic estimation of installation costs also requires reference to local labor rates, site-specific factors, and other case specifics.

LEACHING

General References: Coulson and Richardson, *Chemical Engineering,* 4th ed., vol. 2, Pergamon Press, Oxford, 1991. Duby, "Hydrometallurgy," in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 16, Wiley, New York, 1995, p. 338. McCabe, Smith, and Harriott, *Unit Operations of Chemical Engineering,* 5th ed., McGraw-Hill, New York, 1993, chaps. 17 and 20. Prubhudesal, in Schweitzer, *Handbook of Separation Techniques for Chemical Engineers,* McGraw-Hill, New York, 1979, sec. 5.1. Rickles, *Chem. Eng.* **72**(6): 157 (1965). Schwartzberg (chap. 10, "Leaching—Organic Materials") and Wadsworth (chap. 9, "Leaching—Metals Applications") in Rousseau, *Handbook of Separation Process Technology,* Wiley, New York, 1987. Wakeman, "Extraction (Liquid-Solid)" in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 10, Wiley, New York, 1993, p. 186.

DEFINITION

Leaching is the removal of a soluble fraction, in the form of a solution, from an insoluble, permeable solid phase with which it is associated. The separation usually involves selective dissolution, with or without diffusion, but in the extreme case of simple washing it consists merely of the displacement (with some mixing) of one interstitial liquid by another with which it is miscible. The soluble constituent may be solid or liquid; and it may be incorporated within, chemically combined with, adsorbed upon, or held mechanically in the pore structure of the insoluble material. The insoluble solid may be massive and porous; more often it is particulate, and the particles may be openly porous, cellular with selectively permeable cell walls, or surface-activated.

It is common practice to exclude from consideration as leaching the elution of surface-adsorbed solute. This process is treated instead as a special case of the reverse operation, adsorption. Also usually excluded is the washing of filter cakes, whether in situ or by reslurrying and refiltration.

Because of its variety of applications and its importance to several ancient industries, leaching is known by a number of other names. Among those encountered in chemical engineering practice are extraction, solid-liquid extraction, lixiviation, percolation, infusion, washing, and decantation-settling. The stream of solids being leached and the accompanying liquid is known as the underflow; in hydrometallurgy practice it is called pulp. The solid content of the stream is sometimes called marc (particularly by oil seed processors). The stream of liquid containing the leached solute is the overflow. As it leaves the leaching process it has several optional names: extract, solution, lixiviate, leachate, or miscella.

Mechanism The mechanism of leaching may involve simple physical solution or dissolution made possible by chemical reaction. The rate of transport of solvent into the mass to be leached, or of soluble fraction into the solvent, or of extract solution out of the insoluble material, or some combination of these rates may be significant. A membranous resistance may be involved. A chemical-reaction rate may also affect the rate of leaching.

Inasmuch as the overflow and underflow streams are not immiscible phases but streams based on the same solvent, the concept of equilibrium for leaching is not the one applied in other mass-transfer separations. If the solute is not adsorbed on the inert solid, true equilibrium is reached only when all the solute is dissolved and distributed uniformly throughout the solvent in both underflow and overflow (or when the solvent is uniformly saturated with the solute, a condition never encountered in a properly designed extractor). The practical interpretation of leaching equilibrium is the state in which the overflow and underflow liquids are of the same composition; on a y-x diagram, the equilibrium line will be a straight line through the origin with a slope of unity. It is customary to calculate the number of ideal (equilibrium) stages required for a given leaching task and to adjust the number by applying a stage efficiency factor, although local efficiencies, if known, can be applied stage by stage.

Usually, however, it is not feasible to establish a stage or overall efficiency or a leaching rate index (e.g., overall coefficient) without testing small-scale models of likely apparatus. In fact, the results of such tests may have to be scaled up empirically, without explicit evaluation of rate or quasi-equilibrium indices.

Methods of Operation Leaching systems are distinguished by operating cycle (batch, continuous, or multibatch intermittent); by direction of streams (cocurrent, countercurrent, or hybrid flow); by staging (single-stage, multistage, or differential-stage); and by method of contacting (sprayed percolation, immersed percolation, or solids dispersion). In general, descriptors from all four categories must be assigned to stipulate a leaching system completely (e.g., the Bollman-type extractor is a continuous hybrid-flow multistage sprayed percolator).

Whatever the mechanism and the method of operation, it is clear that the leaching process will be favored by increased surface per unit volume of solids to be leached and by decreased radial distances that must be traversed within the solids, both of which are favored by decreased particle size. Fine solids, on the other hand, cause slow percolation rate, difficult solids separation, and possible poor quality of solid product. The basis for an optimum particle size is established by these characteristics.

LEACHING EQUIPMENT

It is classification by contacting method that provides the two principal categories into which leaching equipment is divided: (1) that in which the leaching is accomplished by percolation and (2) that in which particulate solids are dispersed into a liquid and subsequently separated from it. Each includes batch and continuous units. Materials which disintegrate during leaching are treated in equipment of the second class.

A few designs of continuous machines fall in neither of these major classes.

Percolation In addition to being applied to ores and rock in place and by the simple technique of heap leaching (usually on very large scale; see Wadsworth, loc. cit.); percolation is carried out in batch tanks and in continuous or dump extractors (usually on smaller scale).

Batch Percolators The **batch tank** is not unlike a big nutsche filter; it is a large circular or rectangular tank with a false bottom. The solids to be leached are dumped into the tank to a uniform depth. They are sprayed with solvent until their solute content is reduced to an economic minimum and are then excavated. Countercurrent flow of the solvent through a series of tanks is common, with fresh solvent entering the tank containing most nearly exhausted material. In a typical ore-dressing operation the tanks are 53 by 20 by 5.5 m (175 by 67 by 18 ft) and extract about 8200 Mg (9000 U.S. tons) of ore on a 13-day cycle. Some tanks operate under pressure, to contain volatile solvents or increase the percolation rate. A series of pressure tanks operating with countercurrent solvent flow is called a **diffusion battery.**

Continuous Percolators Coarse solids are also leached by percolation in moving-bed equipment, including single-deck and multideck rake classifiers, bucket-elevator contactors, and horizontal-belt conveyors.

The Bollman-type extractor shown in Fig. 18-76 is a bucket-elevator unit designed to handle about 2000 to 20,000 kg/h (50 to 500 U.S. tons/day) of flaky solids (e.g., soybeans). Buckets with perforated

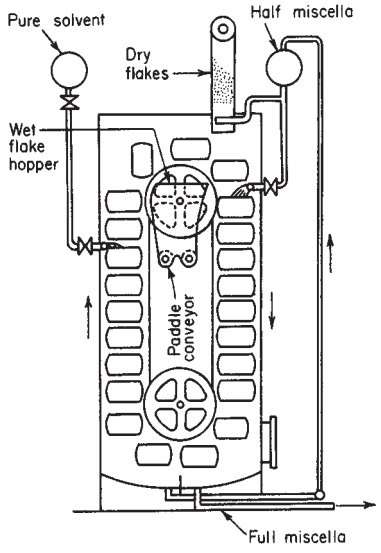


FIG. 18-76 Bollman-type extractor. (*McCabe, Smith, and Harriott,* Unit Operations of Chemical Engineering, *5th ed., p. 616. Copyright 1993 by McGraw-Hill, Inc., New York. Used with permission of McGraw-Hill Book Company.*)

bottoms are held on an endless moving belt. Dry flakes, fed into the descending buckets, are sprayed with partially enriched solvent ("half miscella") pumped from the bottom of the column of ascending buckets. As the buckets rise on the other side of the unit, the solids are sprayed with a countercurrent stream of pure solvent. Exhausted flakes are dumped from the buckets at the top of the unit into a paddle conveyor; enriched solvent, the "full miscella," is pumped from the bottom of the casing. Because the solids are unagitated and because the final miscella moves cocurrently, the Bollman extractor permits the use of thin flakes while producing extract of good clarity. It is only partially a countercurrent device, however, and it sometimes permits channeling and consequent low stage efficiency. Perhaps for this reason, it is being displaced in the oil extraction industry by horizontal basket, pan, or belt percolators (Schwartzberg, loc. cit.).

In the **horizontal-basket design,** illustrated by the **Rotocel extractor** (Fig. 18-77), walled compartments in the form of annular sectors with liquid-permeable floors revolve about a central axis. The compartments successively pass a feed point, a number of solvent sprays, a drainage section, and a discharge station (where the floor opens to discharge the extracted solids). The discharge station is circumferentially contiguous to the feed point. Countercurrent extraction is achieved by feeding fresh solvent only to the last compartment before dumping occurs and by washing the solids in each preceding compartment with the effluent from the succeeding one. The Rotocel is simple and inexpensive, and it requires little headroom. This type of equipment is made by a number of manufacturers. Horizontal table and tilting-pan vacuum filters, of which it is the gravity counterpart, are used as extractors for leaching processes involving difficult solution-residue separation.

The **endless-belt percolator** (Wakeman, loc. cit.) is similar in principle, but the successive feed, solvent spray, drainage, and dumping stations are linearly rather than circularly disposed. Examples are the **de Smet belt extractor** (uncompartmented) and the **Lurgi frame belt** (compartmented), the latter being a kind of linear equivalent of the Rotocel. Horizontal-belt vacuum filters, which resemble endless-belt extractors, are sometimes used for leaching.

The **Kennedy extractor** (Fig. 18-78), also requiring little headroom, operates substantially as a percolator that moves the bed of solids through the solvent rather than the conventional opposite. It comprises a nearly horizontal line of chambers through each of which in succession the solids being leached are moved by a slow impeller enclosed in that section. There is an opportunity for drainage between stages when the impeller lifts solids above the liquid level before dumping them into the next chamber. Solvent flows countercurrently from chamber to chamber. Because the solids are subjected to mechanical action somewhat more intense than in other types of continuous percolator, the Kennedy extractor is now little used for fragile materials such as flaked oil seeds.

Dispersed-Solids Leaching Equipment for leaching fine solids by dispersion and separation includes batch tanks agitated by rotating impellers or by air and a variety of continuous devices.

Batch Stirred Tanks Tanks agitated by coaxial impellers (turbines, paddles, or propellers) are commonly used for batch dissolution of solids in liquids and may be used for leaching fine solids. Insofar as the controlling rate in the mass transfer is the rate of transfer of mate-

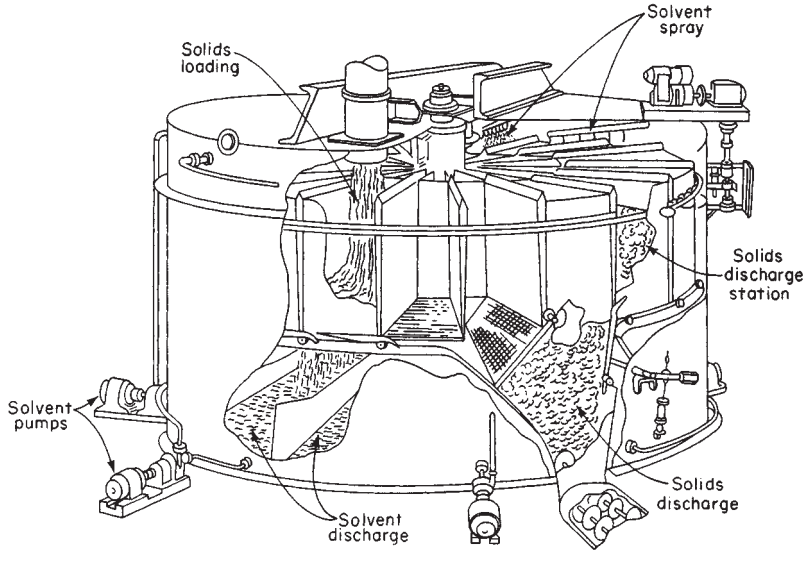


FIG. 18-77 Rotocel extractor. [*Rickles,* Chem. Eng. **72**(6): *164 (1965). Used with permission of McGraw-Hill, Inc.*]

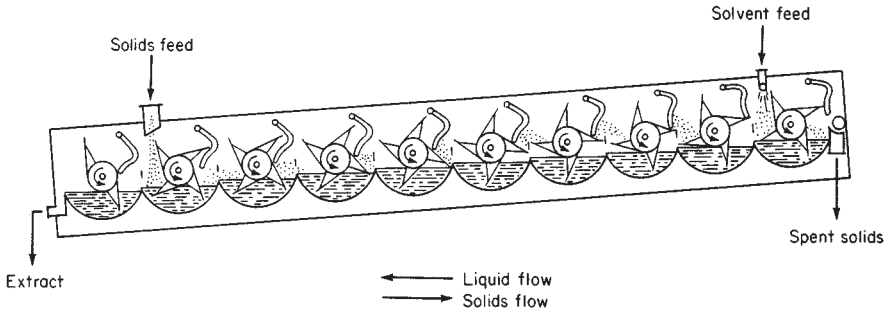


FIG. 18-78 Kennedy extractor. (*Vulcan Cincinnati, Inc.*)

rial into or from the interior of the solid particles rather than the rate of transfer to or from the surface of particles, the main function of the agitator is to supply unexhausted solvent to the particles while they reside in the tank long enough for the diffusive process to be completed. The agitator does this most efficiently if it just gently circulates the solids across the tank bottom or barely suspends them above the bottom.

The leached solids must be separated from the extract by settling and decantation or by external filters, centrifuges, or thickeners, all of which are treated elsewhere in Sec. 18. The difficulty of solids-extract separation and the fact that a batch stirred tank provides only a single equilibrium stage are its major disadvantages.

Pachuca Tanks Ores of gold, uranium, and other metals are commonly batch-leached in large air-agitated vessels known as Pachuca tanks. A typical tank is a vertical cylinder with a conical bottom section usually with a 60° included angle, 7 m (23 ft) in diameter and 14 m (46 ft) in overall height. In some designs air is admitted from an open pipe in the bottom of the cone and rises freely through the tank; more commonly, however, it enters through a central vertical tube, characteristically about 46 cm (18 in) in diameter, that extends from the bottom of the tank to a level above the conical section—in some cases, almost to the liquid surface. Before it disengages at the liquid surface, the air induces in and above the axial tube substantial flow of pulp, which then finds its way down the outer part of the tank, eventually reentering the riser. The circulation rate in Pachuca tanks is discussed by Lamont [*Can. J. Chem. Eng.*, **36,** 153 (1958)].

Continuous Dispersed-Solids Leaching

Vertical-plate extractor. Exemplified by the **Bonotto extractor** (Fig. 18-79), this consists of a column divided into cylindrical compartments by equispaced horizontal plates. Each plate has a radial opening staggered 180° from the openings of the plates immediately above and below it, and each is wiped by a rotating radial blade. Alternatively, the plates may be mounted on a coaxial shaft and rotated past stationary blades. The solids, fed to the top plate, thus are caused to fall to each lower plate in succession. The solids fall as a curtain into solvent which flows upward through the tower. They are discharged by a screw conveyor and compactor. Like the Bollman extractor, the Bonotto has been virtually displaced by horizontal belt or tray percolators for the extraction of oil seeds.

Gravity sedimentation tanks. Operated as thickeners, these tanks can serve as continuous contacting and separating devices in which fine solids may be leached continuously. A series of such units properly connected permit true continuous countercurrent washing of fine solids. If appropriate, a mixing tank may be associated with each thickener to improve the contact between the solids and liquid being fed to that stage. Gravity sedimentation thickeners are described under "Gravity Sedimentation Operations." Of all continuous leaching equipment, gravity thickeners require the most area, and they are limited to relatively fine solids.

The Dorr agitator (Coulson and Richardson, loc. cit.) consolidates in one unit the principles of the thickener and the Pachuca tank. Resembling a rake-equipped thickener, it differs in that the rake is driven by a hollow shaft through which the solids-liquid suspension is lifted and circulated by an air stream. The rake moves the pulp to the center, where it can be entrained by the air stream. The unit may be operated batchwise or continuously.

Impeller-agitated tanks. These can be operated as continuous leaching tanks, singly or in a series. If the solids feed is a mixture of particles of different settling velocities and if it is desirable that all particles reside in the leaching tank the same lengths of time, design of a continuous stirred leach tank is difficult and uncertain.

Screw-Conveyor Extractors One type of continuous leaching equipment, employing the screw-conveyor principle, is strictly speaking neither a percolator nor a dispersed-solids extractor. Although it is often classed with percolators, there can be sufficient agitation of the solids during their conveyance by the screw that the action differs from an orthodox percolation.

The **Hildebrandt total-immersion extractor** is shown schematically in Fig. 18-80. The helix surface is perforated so that solvent can pass through countercurrently. The screws are so designed to compact

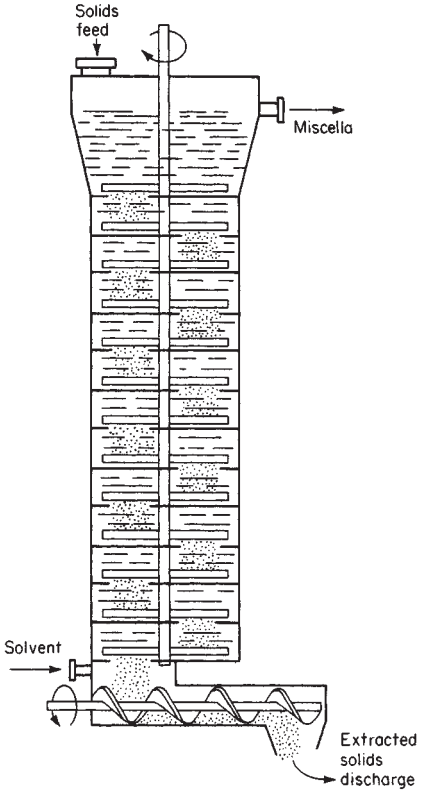


FIG. 18-79 Bonotto extractor. [*Rickles,* Chem. Eng. ***72****(6): 163 (1965); copyright 1965 by McGraw-Hill, Inc., New York. Excerpted with special permission of McGraw-Hill.*]

the solids during their passage through the unit. The design offers the obvious advantages of countercurrent action and continuous solids compaction, but there are possibilities of some solvent loss and feed overflow, and successful operation is limited to light, permeable solids.

A somewhat similar but simpler design uses a horizontal screw section for leaching and a second screw in an inclined section for washing, draining, and discharging the extracted solids.

In the **De Danske Sukkerfabriker,** the axis of the extractor is tilted to about 10° from the horizontal, eliminating the necessity of two screws at different angles of inclination.

Sugar-beet cossettes are successfully extracted while being transported upward in a vertical tower by an arrangement of inclined plates or wings attached to an axial shaft. The action is assisted by staggered guide plates on the tower wall. The shell is filled with water that passes downward as the beets travel upward. This configuration is employed in the **BMA diffusion tower** (Wakeman, loc. cit.).

Schwartzberg (loc. cit.) reports that screw-conveyor extractors, once widely employed to extract flaked oil seeds, have fallen into disuse for this application because of their destructive action on the fragile seed flakes.

Tray Classifier A hybrid like the screw-conveyor classifier, the tray classifier rakes pulp up the sloping bottom of a tank while solvent flows in the opposite direction. The solvent is forced by a baffle to the bottom of the tank at the lower end before it overflows. The solids must be rugged enough to stand the stress of raking.

SELECTION OR DESIGN OF A LEACHING PROCESS*

At the heart of a leaching plant design at any level—conceptual, preliminary, firm engineering, or whatever—is unit-operations and process design of the extraction unit or line. The major aspects that are particular for the leaching operation are the selection of process and operating conditions and the sizing of the extraction equipment.

Process and Operating Conditions The major parameters that must be fixed or identified are the solvent to be used, the temperature, the terminal stream compositions and quantities, leaching cycle (batch or continuous), contact method, and specific extractor choice.

Choice of Solvent The solvent selected will offer the best balance of a number of desirable characteristics: high saturation limit and selectivity for the solute to be extracted, capability to produce extracted material of quality unimpaired by the solvent, chemical stability under process conditions, low viscosity, low vapor pressure, low toxicity and flammability, low density, low surface tension, ease and economy of recovery from the extract stream, and price. These factors are listed in an approximate order of decreasing importance, but the specifics of each application determine their interaction and relative significance, and any one can control the decision under the right combination of process conditions.

Temperature The temperature of the extraction should be chosen for the best balance of solubility, solvent-vapor pressure, solute diffusivity, solvent selectivity, and sensitivity of product. In some cases, temperature sensitivity of materials of construction to corrosion or erosion attack may be significant.

Terminal Stream Compositions and Quantities These are basically linked to an arbitrary given: the production capacity of the leaching plant (rate of extract production or rate of raw-material purification by extraction). When options are permitted, the degree of solute removal and the concentration of the extract stream chosen are those that maximize process economy while sustaining conformance to regulatory standards.

Leaching Cycle and Contact Method As is true generally, the choice between continuous and intermittent operation is largely a matter of the size and nature of the process of which the extraction is a part. The choice of a percolation or solids-dispersion technique depends principally on the amenability of the extraction to effective, sufficiently rapid percolation.

Type of Reactor The specific type of reactor that is most compatible (or least incompatible) with the chosen combination of the preceding parameters seldom is clearly and unequivocally perceived without difficulty, if at all. In the end, however, that remains the objective. As is always true, the ultimate criteria are reliability and profitability.

Extractor-Sizing Calculations For any given throughput rate (which fixes the cross-sectional area and/or the number of extractors), the size of the units boils down to the number of stages required, actual or equivalent. In calculation, this resolves into determination of the number of ideal stages required and application of appropriate stage efficiencies. The methods of calculation resemble those for other mass-transfer operations (see Secs. 13, 14, and 15), involving equilibrium data and contact conditions, and based on material balances. They are discussed briefly here with reference to countercurrent contacting.

Composition Diagrams In its elemental form, a leaching system consists of three components: inert, insoluble solids; a single nonadsorbed solute, which may be liquid or solid; and a single solvent.* Thus, it is a ternary system, albeit an unusual one, as already mentioned, by virtue of the total mutual "insolubility" of two of the phases and the simple nature of equilibrium.

The composition of a typical system is satisfactorily presented in the form of a diagram. Those diagrams most frequently employed are a right-triangular plot of mass fraction of solvent against mass fraction of solute (Fig. 18-81*a*) and a plot suggestive of a Ponchon-Savarit diagram, with inerts taking the place of enthalpy (Fig. 18-81*b*). A third diagram, less frequently used, is a modified McCabe-Thiele plot in which the overflow solution (inerts-free) and the underflow solution (traveling out of a stage with the inerts) are treated as pseudo phases, the mass fraction of solute in overflow, y, being plotted against the mass fraction of solute in underflow, x. (An additional representation, the equilateral-triangular diagram frequently employed for liquid-liquid ternary systems, is seldom used because the field of leaching data is confined to a small portion of the triangle.)

With reference to Fig. 18-81 (both graphs), EF represents the locus of overflow compositions for the case in which the overflow stream contains no inert solids. $E'F'$ represents the overflow streams containing some inert solids, either by entrainment or by partial solubility in the overflow solution. Lines GF, GL, and GM represent the loci of underflow compositions for the three different conditions indicated on the diagram. In Fig. 18-81*a*, the constant underflow line GM is parallel to EF, the hypotenuse of the triangle, whereas GF passes through

* Portions of this subsection are adaptations from the still-pertinent article by Rickles (loc. cit.).

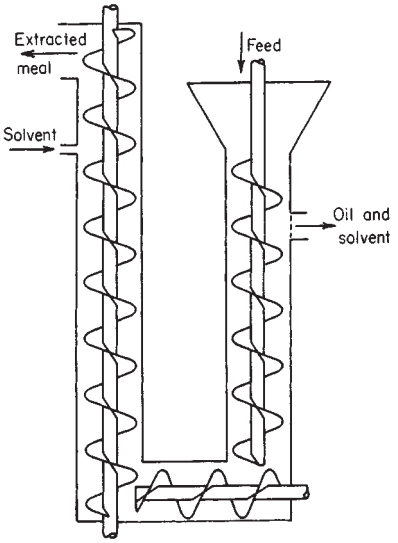


FIG. 18-80 Hildebrandt extractor. (*McCabe, Smith, and Harriott,* Unit Operations of Chemical Engineering, *5th ed., p. 616. Copyright 1993 by McGraw-Hill, Inc., New York. Used with permission by McGraw-Hill Book Company.*)

* The solubility of the inert, adsorption of solute on the inert, and complexity of solvent and extracted material can be taken into account if necessary. Their consideration is beyond the scope of this treatment.

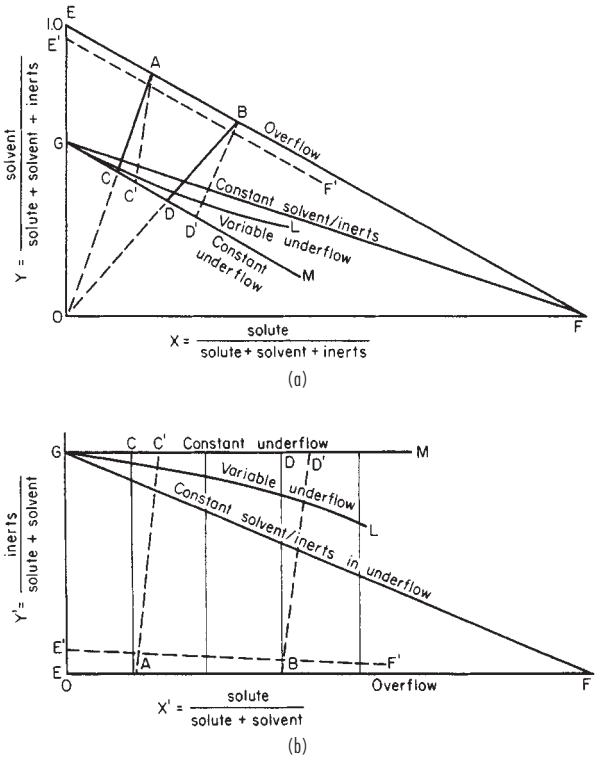


FIG. 18-81 Composition diagrams for leaching calculations: (*a*) right-triangular diagram; (*b*) modified Ponchon-Savarit diagram.

the right-hand vertex representing 100 percent solute. In Fig. 18-81*b*, underflow line *GM* is parallel to the abscissa, and *GF* passes through the point on the abscissa representing the composition of the clear solution adhering to the inert solids.

Compositions of overflow and underflow streams leaving the same stage are represented by the intersection of the composition lines for those streams with a tie line (*AC*, *AC′*, *BD*, *BD′*). Equilibrium tie lines (*AC*, *BD*) pass through the origin (representing 100 percent inerts) in Fig. 18-81*a*, and are vertical (representing the same inert-free solution composition in both streams) in Fig. 18-81*b*. For nonequilibrium conditions with or without adsorption or for equilibrium conditions with selective adsorption, the tie lines are displaced, such as *AC′* and *BD′*. Point *C′* is to the right of *C* if the solute concentration in the overflow solution is less than that in the underflow solution adhering to the solids. Unequal concentrations in the two solutions indicate insufficient contact time and/or preferential adsorption of one of the components on the inert solids. Tie lines such as *AC′* may be considered as "practical tie lines" (i.e., they represent actual rather than ideal stages) if data on underflow and overflow composition have been obtained experimentally under conditions simulating actual operation, particularly with respect to contact time, agitation, and particle size of solids.

The illustrative construction lines of Fig. 18-81 have been made with the assumption of constant underflow. In the more realistic case of variable underflow, the points *C*, *C′*, *D*, *D′* would lie along line *GL*. Like the practical tie lines, *GL* is a representation of experimental data.

Algebraic Computation This method starts with calculation of the quantities and compositions of all the terminal streams, using a convenient quantity of one of the streams as the basis of calculation. Material balance and stream compositions are then computed for a terminal ideal stage at either end of an extraction battery (i.e., at Point *A* or Point *B* in Fig. 18-81), using equilibrium and solution-retention data. Calculations are repeated for each successive ideal stage from one end of the system to the other until an ideal stage which corresponds to the desired conditions is obtained. Any solid-liquid extraction problem can be solved by this method.

For certain simplified cases it is possible to calculate directly the number of stages required to attain a desired product composition for a given set of feed conditions. For example, if equilibrium is attained in all stages and if the underflow mass rate is constant, both the equilibrium and operating lines on a modified McCabe-Thiele diagram are straight, and it is possible to calculate directly the number of ideal stages required to accommodate any rational set of terminal flows and compositions (McCabe, Smith, and Harriott, op. cit.):

$$N = \frac{\log\left[(y_b - x_b)/(y_a - x_a)\right]}{\log\left[(y_b - y_a)/(x_b - x_a)\right]} \qquad (18\text{-}42)$$

Even when the conditions of equilibrium in each stage and constant underflow obtain, Eq. (18-42) normally is not valid for the first stage because the unextracted solids entering that stage usually are not premixed with solution to produce the underflow mass that will leave. This is easily rectified by calculating the exit streams for the first stage and using those values in Eq. (18-42) to calculate the number of stages required after stage 1.

Graphical Method This method of calculation is simply a diagrammatic representation of all the possible compositions in a leaching system, including equilibrium values, on which material balances across ideal (or, in some cases, nonideal) stages can be evaluated in the graphical equivalent of the stage-by-stage algebraic computation. It normally is simpler than the hand calculation of the algebraic solution, and it is viewed by many as helpful because it permits visualization of the process variables and their effect on the operation. Any of the four types of composition diagrams described above can be used, but modified Ponchon-Savarit or right-triangular plots (Fig. 18-81) are most convenient for leaching calculations.

The techniques of graphical solution, in fact, are not unlike those for distillation and absorption (binary) problems using McCabe-Thiele, Ponchon-Savarit, and right-triangular diagrams and are similar to those described in Sec. 15 for solvent-extraction (ternary) systems. More detailed explanations of the application of the several graphical conventions to leaching are presented by: Coulson and Richardson, right triangle; Rickles, modified Ponchon-Savarit; McCabe, Smith, and Harriott, modified McCabe-Thiele; and Schwartzberg, equilateral ternary diagram; all in the publications cited as general references. (See also Treybal, *Mass Transfer Operations,* 3d ed., McGraw-Hill, New York, 1980.)

GRAVITY SEDIMENTATION OPERATIONS

GENERAL REFERENCES: Albertson, *Fluid/Particle Separation Journal,* **7**(1), 18 (1994). Coe and Clevenger, *Trans. Am. Inst. Min. Eng.,* **55,** 356 (1916). Comings, Pruiss, and DeBord, *Ind. Eng. Chem.,* **46,** 1164 (1954). Counselmann, *Trans. Am. Inst. Min. Eng.,* **187,** 223 (1950). Fitch, *Ind. Eng. Chem.,* **58**(10), 18 (1966). *Trans. Soc. Min. Eng. AIME,* **223,** 129 (1962). Kynch, *Trans. Faraday Soc.,* **48,** 166 (1952). Pearse, *Gravity Thickening Theories: A Review,* Warren Spring Laboratory, Hertfordshire, 1977. Purchas, *Solid/Liquid Separation Equipment Scale-Up,* Uplands Press, Croydon, England, 1977. Sankey and Payne, *Chemical Reagents in the Mineral Processing Industry,* **245,** SME (1985). Talmage and Fitch, *Ind. Eng. Chem.,* **47,** 38 (1955). Wilhelm and Naide, *Min. Eng. (Littleton, Colo.),* **33,** 1710 (1981).

Sedimentation is the partial separation or concentration of suspended solid particles from a liquid by gravity settling. This field may be divided into the functional operations of thickening and clarification. The primary purpose of thickening is to increase the concentration of suspended solids in a feed stream, while that of clarification is to

remove a relatively small quantity of suspended particles and produce a clear effluent. These two functions are similar and occur simultaneously, and the terminology merely makes a distinction between the primary process results desired. Generally, thickener mechanisms are designed for the heavier-duty requirements imposed by a large quantity of relatively concentrated pulp, while clarifiers usually will include features that ensure essentially complete suspended-solids removal, such as greater depth, special provision for coagulation or flocculation of the feed suspension, and greater overflow-weir length.

CLASSIFICATION OF SETTLEABLE SOLIDS; SEDIMENTATION TESTS

The types of sedimentation encountered in process technology will be greatly affected not only by the obvious factors—particle size, liquid viscosity, solid and solution densities—but also by the characteristics of the particles within the slurry. These properties, as well as the process requirements, will help determine both the type of equipment which will achieve the desired ends most effectively and the testing methods to be used to select the equipment.

Figure 18-82 illustrates the relationship between solids concentration, interparticle cohesiveness, and the type of sedimentation that may exist. "Totally discrete" particles include many mineral particles (usually greater in diameter than 20 μm), salt crystals, and similar substances that have little tendency to cohere. "Flocculent" particles generally will include those smaller than 20 μm (unless present in a dispersed state owing to surface charges), metal hydroxides, many chemical precipitates, and most organic substances other than true colloids.

At low concentrations, the type of sedimentation encountered is called particulate settling. Regardless of their nature, particles are sufficiently far apart to settle freely. Faster-settling particles may collide with slower-settling ones and, if they do not cohere, continue downward at their own specific rate. Those that do cohere will form floccules of a larger diameter that will settle at a rate greater than that of the individual particles.

There is a gradual transition from particulate settling into the zone-settling regime, where the particles are constrained to settle as a mass. The principal characteristic of this zone is that the settling rate of the mass, as observed in batch tests, will be a function of its solids concentration (for any particular condition of flocculation, particle density, etc.).

The solids concentration ultimately will reach a level at which particle descent is restrained not only by hydrodynamic forces but also partially by mechanical support from the particles below; therefore, the weight of particles in mutual contact can influence the rate of sedimentation of those at lower levels. This compression, as it is termed, will result in further solids concentration because of compaction of the individual floccules and partial filling of the interfloc voids by the deformed floccules. Accordingly, the rate of sedimentation in the compression regime is a function of both the solids concentration and the depth of pulp in this particular zone. As indicated in Fig. 18-82, granular, nonflocculent particles may reach their ultimate solids concentration without passing through this regime.

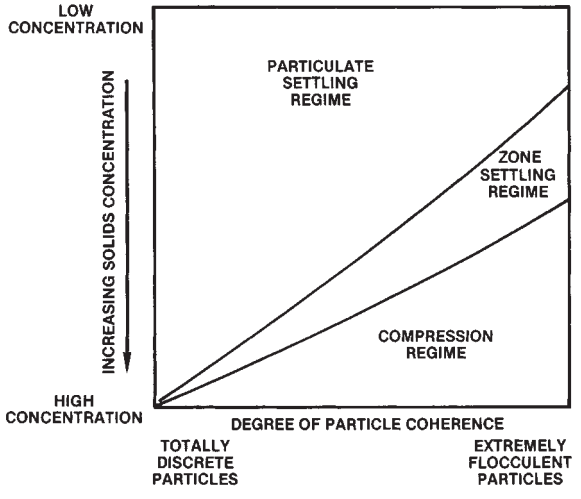


FIG. 18-82 Combined effect of particle coherence and solids concentration on the settling characteristics of a suspension.

As an illustration, coarse-size (45 μm) the aluminum oxide trihydrate particles produced in the Bayer process would be located near the extreme left of Fig. 18-82. These solids settle in a particulate manner, passing through a zone-settling regime only briefly, and reach a terminal density or ultimate solids concentration without any significant compressive effects. At this point, the solids concentration may be as much as 80 percent by weight. The same compound, but of the gelatinous nature it has when precipitated in water treatment as aluminum hydroxide, would be on the extreme right-hand side of the figure. This flocculent material enters into a zone-settling regime at a low concentration (relative to the ultimate concentration it can reach) and gradually thickens. With sufficient pulp depth present, preferably aided by gentle stirring or vibration, the compression-zone effect will occur; this is essential for the sludge to attain its maximum solids concentration, around 10 percent. Certain fine-size (1- to 2-μm) precipitates of this compound will possess characteristics intermediate between the two extremes.

A feed stream to be clarified or thickened can exist at any state represented within this diagram. As it becomes concentrated owing to sedimentation, it may pass through all the regimes, and the settling rate in any one may be the size-determining factor for the required equipment.

Sedimentation-Test Procedures

Determination of Clarification-Zone Requirements In the treatment of solids suspensions which are in the particulate-settling regime, the usual objective will be the production of a clear effluent and test methods limited to this type of settling will be the normal sizing procedure, although the area demand for thickening should be verified. With particulate or slightly flocculent matter, any method that measures the rate of particle subsidence will be suitable, and either long-tube or short-tube procedures (described later) may be used. If the solids are strongly flocculent and particles cohere easily during sedimentation, the long tube test will yield erratic data, with better clarities being observed in samples taken from the lower taps (i.e., clarity appears to improve at higher settling rates). In these instances, time alone usually is the principal variable in clarification, and a simple detention test is recommended.

Long-Tube Method A transparent tube 2 to 4 m long and at least 100 mm in diameter (preferably larger), fitted with sampling taps every 200 to 300 mm, is used in this test. The tube is mounted vertically and filled with a representative sample of feed suspension. At timed intervals approximately 100-mL samples are withdrawn from successive taps, beginning with the uppermost one. The time intervals will be determined largely by the settling rate of the particles and should be chosen so that a series of at least four time intervals will produce samples that bracket the desired solids-removal target. Also, this procedure will indicate whether or not detention time is a factor in the rate of clarification. Typically, intervals may be 30 min long, the last series of samples representing the results obtainable with 2-h detention. The samples are analyzed for suspended-solids concentration by any suitable means, such as filtration through membranes or centrifugation with calibrated tubes.

A plot is made of the suspended-solids concentration in each of the samples as a function of the nominal settling velocity of the sample, which is determined from the corresponding sample-tap depth divided by the elapsed time between the start of the test and the time of sampling. For each sampling series after the first, the depth will have changed because of the removal of the preceding samples, and this must be taken into account. With particulate solids having little or no tendency to cohere, the data points generally will fall on one line irrespective of the detention time. This indicates that the settling area

available in the basin will determine the degree of solids removal, and the depth will have little bearing on the results, except as it may affect clarification efficiency.

Since the solids concentration in the 100-mL samples withdrawn at different depths does not correspond to the average concentration in the fluid above the sample point (which would be equivalent to the overflow from the clarifier at that particular design rate), an adjustment must be made in calculating the required area. Accordingly, an approximate average of the solids concentration throughout the column of liquid above a given tap can be obtained by summing the values obtained from all the higher taps and the one which is being sampled and dividing by the total number of taps sampled. This value is then used in a plot of overflow suspended-solids concentration versus nominal settling velocity.

Areal efficiencies for properly designed clarifiers in which detention time is not a significant factor range from 65 to 80 percent, and the surface area should be increased accordingly to reduce the overflow rate for scale-up.

Should the particles have a tendency to cohere slightly during sedimentation, each sampling time, representing a different nominal detention time in the clarifier, will produce different suspended-solids concentrations at similar rates. These data can be plotted as sets of curves of concentration versus settling rate for each detention time by the means just described. Scale-up will be similar, except that detention time will be a factor, and both depth and area of the clarifier will influence the results. In most cases, more than one combination of diameter and depth will be capable of producing the same clarification result.

These data may be evaluated by selecting different nominal overflow rates (equivalent to settling rates) for each of the detention-time values, and then plotting the suspended-solids concentrations for each nominal overflow rate (as a parameter) against the detention time. For a specified suspended-solids concentration in the effluent, a curve of overflow rate versus detention time can be prepared from this plot and used for optimizing the design of the equipment.

Short-Tube Method This test is suitable in cases in which detention time does not change the degree of particle flocculation and hence has no significant influence on particle-settling rates. It is also useful for hydroseparator tests where the sedimentation device is to be used for classification (see Sec. 19). A tube 50 to 75 mm in diameter and 300 to 500 mm long is employed. A sample placed in the tube is mixed to ensure uniformity, and settling is allowed to occur for a measured interval. At the end of this time, the supernatant liquid is siphoned off quickly down to a chosen level, and the collected sample is analyzed for suspended-solids concentration. The level selected usually is based on the relative expected volumes of overflow and underflow. The suspended-solids concentration measured in the siphoned sample will be equivalent to the "averaged" values obtained in the long-tube test, at a corresponding settling rate.

In hydroseparator tests, it is necessary to measure solids concentrations and size distributions of both the supernatant sample withdrawn and the fraction remaining in the cylinder. The volume of the latter sample should be such as to produce a solids concentration that would be typical of a readily pumped underflow slurry.

Detention Test This test utilizes a 1- to 4-L beaker or similar vessel. The sample is placed in the container, flocculated by suitable means if required, and allowed to settle. Small samples for suspended-solids analysis are withdrawn from a point approximately midway between liquid surface and settled solids interface, taken with sufficient care that settled solids are not resuspended. Sampling times may be at consecutively longer intervals, such as 5, 10, 20, 40, and 80 min.

The suspended-solids concentration can be plotted on log-log paper as a function of the sampling (detention) time. A straight line usually will result, and the required static detention time t to achieve a certain suspended-solids concentration C in the overflow of an ideal basin can be taken directly from the graph. If the plot is a straight line, the data are described by the equation

$$C = Kt^m \tag{18-43}$$

where the coefficient K and exponent m are characteristic of the particular suspension.

Should the suspension contain a fraction of solids which can be considered "unsettleable," the data are more easily represented by using the so-called second-order procedure. This depends on the data being reasonably represented by the equation

$$Kt = \frac{1}{C - C_\infty} - \frac{1}{C_0 - C_\infty} \tag{18-44}$$

where C_∞ is the unsettleable-solids concentration and C_0 is the concentration of suspended solids in the unsettled (feed) sample. The residual-solids concentration remaining in suspension after a sufficiently long detention time (C_∞) must be determined first, and the data then plotted on linear paper as the reciprocal concentration function $1/(C - C_\infty)$ versus time.

Bulk-settling test. In cases involving detention time only, the overflow rate must be considered by other means. This is done by carrying out a settling test in which the solids are first concentrated to a level at which zone settling just begins. This is usually marked by a very diffuse interface during initial settling. Its rate of descent is measured with a graduated cylinder of suitable size, preferably at least 1 L, and the initial straight-line portion of the settling curve is used for specifying a bulk-settling rate. The design overflow rate generally should not exceed half of the bulk-settling rate.

Detention efficiency. Conversion from the ideal basin sized by detention-time procedures to an actual clarifier requires the inclusion of an efficiency factor to account for the effects of turbulence and nonuniform flow. Efficiencies vary greatly, being dependent not only on the relative dimensions of the clarifier and the means of feeding but also on the characteristics of the particles. The curve shown in Fig. 18-83 can be used to scale up laboratory data in sizing circular clarifiers. The static detention time determined from a test to produce a specific effluent solids concentration is divided by the efficiency (expressed as a fraction) to determine the nominal detention time, which represents the volume of the clarifier above the settled pulp interface divided by the overflow rate. Different diameter-depth combinations are considered by using the corresponding efficiency factor. In most cases, area may be determined by factors other than the bulk-settling rate, such as practical tank-depth limitations.

Thickener-Basin Area The area requirements for thickeners frequently are based on the solids flux rates measured in the zone-settling regime. Theory holds that, for any specific sedimentation condition, a critical concentration which will limit the solids throughput rate will exist in the thickener. This critical concentration will be evidenced as a pulp bed of variable depth in which the solids concentration is fairly uniform from top to bottom. Since the underflow concentration usually will be higher than this, gradually increasing concentrations will be found with progressing depth in the region beneath this constant-concentration zone. As the concentration within this critical zone represents a steady-state condition, its vertical extent may vary continually, responding to minor changes in the feed rate, underflow withdrawal rate, or flocculant dosage. In thickeners operating at relatively high underflow concentrations, with long

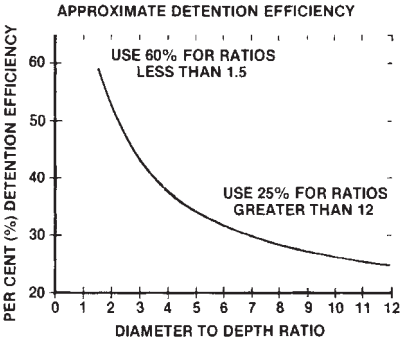


FIG. 18-83 Efficiency curve for scale-up of barch clarification data to determine nominal detention time in a continuous clarifier.

solids-detention times and lower throughput, this zone generally will not be present.

Many batch-test methods which are based on determining the solids flux rate at this critical concentration have been developed. Most methods recognize that as the solids enter compression, thickening behavior is no longer a function only of solids concentration. Hence, these methods attempt to utilize the "critical" point dividing these two zones and size the area on the basis of the settling rate of a layer of pulp at this concentration. The difficulty lies in discerning where this point is located on the settling curve.

Many procedures have been developed, but two in particular have been more widely used: the Coe and Clevenger approach and the Kynch method as defined by Talmage and Fitch (op. cit.).

The former requires measurement of the initial settling rate of a pulp at different solids concentrations varying from feed to final underflow value. The area requirement for each solids concentration tested is calculated by equating the net overflow rate to the corresponding interfacial settling rate, as represented by the following equation for the unit area:

$$\text{Unit area} = \frac{1/C_i - 1/C_u}{v_i} \qquad (18\text{-}45)$$

where C_i is the solids concentration at the interfacial settling velocity v_i and C_u is the underflow concentration, both concentrations being expressed in terms of mass of solids per unit volume of slurry. Using kg/L for the concentrations and m/day for the settling velocity yields a unit area value in m^2/(ton/day).

These unit area values, plotted as a function of the feed concentration, will describe a maximum value that can be used to specify the thickener design unit area for the particular underflow concentration C_u employed in Eq. (18-45).

The method is applicable for *unflocculated* pulps or those in which the ionic characteristics of the solution produce a flocculent structure. If polymeric flocculants are used, the floccule size will be highly dependent on the feed concentration, and an approach based on the Kynch theory is preferred. In this method, the test is carried out at the expected feed solids concentration and is continued until underflow concentration is achieved in the cylinder. To determine the unit area, Talmage and Fitch (op. cit.) proposed an equation derived from a relationship equivalent to that shown in Eq. (18-45):

$$\text{Unit area} = \frac{t_u}{C_0 H_0} \qquad (18\text{-}46)$$

where t_u is the time, days; C_0 is the initial solids concentration in the feed, t/m^3; and H_0 is the initial height of the slurry in the test cylinder, m. The term t_u is taken from the intersection of a tangent to the curve at the critical point and a horizontal line representing the depth of pulp at underflow concentration. There are various means for selecting this critical point, all of them empirical, and the unit area value determined cannot be considered precise. The review by Pearse (op. cit.) presents many of the different procedures used in applying this approach to laboratory settling test data.

Because this method in itself does not adequately address the effect of different underflow concentrations on the unit area, a thickener sized using this approach could be too small in a case where a relatively concentrated underflow is desired.

Two other approaches avoid using the critical point by computing the area requirements from the settling conditions existing at the underflow concentration. The Wilhelm and Naide procedure (op. cit.) applies zone-settling theory (Kynch) to the entire thickening regime. Tangents drawn to the settling curve are used to calculate the settling velocity at all concentrations obtained in the test. This permits construction of a plot (Figure 18-84) showing unit area as a function of underflow concentration.

A second, "direct" approach which yields a similar result, since it also takes compression into account, utilizes the value of settling time t_x taken from the settling curve at a particular underflow concentration. This value is used to solve the Talmage and Fitch equation (18-46) for unit area.

Compression bed depth will have a significant effect on the overall settling rate (increasing compression zone depth reduces unit area).

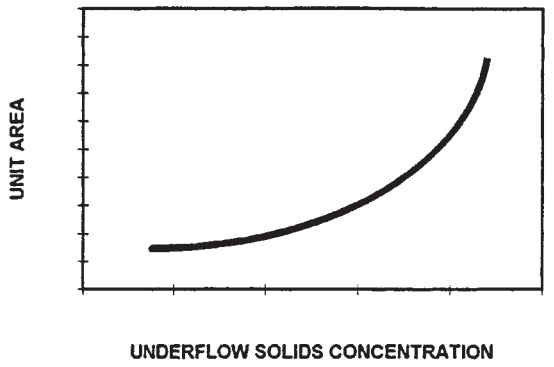


FIG. 18-84 Characteristic relationship between thickener unit area and underflow solids concentration (fixed flocculant dosage and pulp depth).

Therefore, in applying either of these two procedures it is necessary to run the test in a vessel having an average bed depth close to that expected in a full-scale thickener. This requires a very large sample, and it is more convenient to carry out the test in a cylinder having a volume of 1 to 4 liters. The calculated unit area value from this test can be extrapolated to full-scale depth by carrying out similar tests at different depths to determine the effect on unit area. Alternatively, an empirical relationship can be used which is effective in applying a depth correction to laboratory cylinder data over normal operating ranges. The unit area calculated by either the Wilhelm and Naide approach or the direct method is multiplied by a factor equal to $(h/H)^n$, where h is the average depth of the pulp in the cylinder, H is the expected full-scale compression zone depth, usually taken as 1 m, and n is the exponent calculated from Fig. 18-85. For conservative design purposes, the minimum value of this factor that should be used is 0.25.

It is essential to use a slow-speed (approximately 0.1 r/min) picket rake in all cylinder tests to prevent particle bridging and allow the sample to attain the underflow density which is obtainable in a full-scale thickener.

Continuously operated, small-scale or pilot-plant thickeners, ranging from 75 mm diameter by 400 mm depth to several meters in diameter, are also effectively used for sizing full-scale equipment. This approach requires a significantly greater volume of sample, such as

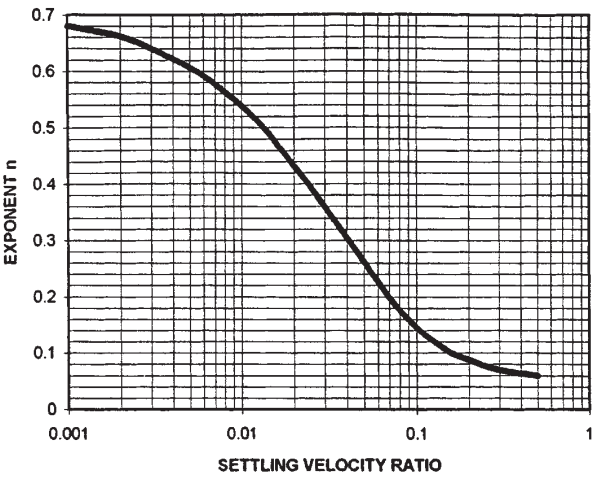


FIG. 18-85 Depth correction factor to be applied to unit areas determined with Wilhelm-Naide and "direct" methods. Velocity ratio calculated using tangents to settling curve at a particular settled solids concentration and at start of test.

would be available in an operating installation or a pilot plant. Continuous units and batch cylinders will produce equivalent results if proper procedures are followed with either system.

Thickener-Basin Depth The pulp depth required in the thickener will be greatly affected by the role that compression plays in determining the rate of sedimentation. If the zone-settling conditions define the area needed, then depth of pulp will be unimportant and can be largely ignored, as the "normal" depth found in the thickener will be sufficient. On the other hand, with the compression zone controlling, depth of pulp will be significant, and it is essential to measure the sedimentation rate under these conditions.

To determine the compression-zone requirement in a thickener, a test should be run in a deep cylinder in which the average settling pulp depth approximates the depth anticipated in the full-scale basin. The average density of the pulp in compression is calculated and used in Eq. (18-47) to determine the required compression-zone volume:

$$V = \frac{\theta_c(\rho_s - \rho_l)}{\rho_s(\rho_{sl} - \rho_l)} \qquad (18\text{-}47)$$

where V is the volume, m^3, required per ton of solids per day; θ_c is the compression time, days, required in the test to reach underflow concentration; and ρ_s, ρ_l, ρ_{sl}, are the densities of the solids, liquid, and slurry (average), respectively, ton/m^3. This value divided by the average depth of the pulp during the period represents the unit area defined by compression requirements. If it exceeds the value determined from the zone-settling tests, it is the quantity to be used.

The side depth of the thickener is determined as the sum of the depths needed for the compression zone and for the clear zone. Normally, 1.5 to 2 m of clear liquid depth above the expected pulp level in a thickener will be sufficient for stable, effective operation. When the location of the pulp level cannot be predicted in advance or it is expected to be relatively low, a thickener sidewall depth of 2 to 3 m is usually safe. Greater depth may be used in order to provide better clarity, although in most thickener applications the improvement obtained by this means will be marginal.

Scale-up Factors Factors used in thickening will vary, but, typically, a 1.2 to 1.3 multiplier applied to the unit area calculated from laboratory data is sufficient if proper testing procedures have been followed and the samples are representative.

Flocculation Flocculants are commonly used because of the considerable reduction in equipment size and capital cost that can be effected with very nominal reagent dosages. Selection of the reagents usually involves simple bench-scale comparison tests on small samples of pulp for rough screening, followed by larger-scale tests in cylinders or in continuous pilot-plant thickeners. Determination of the optimum dosage is complicated; it involves a number of economic factors such as reagent and capital costs, cost of a shutdown or loss in availability due to failure in the flocculation system, and consideration of possible future increases in plant capacity.

Polymeric flocculants are available in various chemical compositions and molecular weight ranges, and they may be nonionic in character or may have predominantly cationic or anionic charges. The range of application varies; but, in general, nonionics are well suited to acidic suspensions, anionic flocculants work well in neutral or alkaline environments, and cationics are most effective on organic material and colloidal matter.

Colloidal solids (e.g., as encountered in waste treatment) may require initial treatment with a chemical having strong ionic properties, such as acid, lime, alum, or ferric sulfate. The latter two will precipitate at neutral pH and produce a gelatinous, flocculent structure which further helps collect extremely small particles. Some cationic polymers also may be effective in flocculation of particles of this type. (This action is commonly termed *coagulation.*) Prolonged, gentle agitation improves the degree and rate of flocculation under these conditions. If the solids concentration is relatively low, e.g., <500 mg/L, results can usually be improved by recirculation of settled material to the flocculation zone to produce an optimum concentration for floc growth.

With polymer flocculation of slurries, however, extended agitation after the addition of the polymer may be detrimental. The reagent should be added to the slurry under conditions which promote rapid dispersion and uniform, complete mixing with a minimum of shear. In cylinder tests, this can be accomplished by simultaneously injecting and mixing flocculant with the slurry, using an apparatus consisting of a syringe, a tube, and an inverted rubber stopper. The stopper, with a diameter approximately three-fourths of that of the cylinder, provides sufficient turbulence as it is moved gently up and down through the sample to cause good blending of reagent and pulp.

Flocculant solution preparation and use should take into account specific properties of these reagents. During mixing and distribution, excessive shear should be avoided since it can reduce reagent effectiveness and result in higher consumption. Flocculant solution should be prepared at as high a concentration—generally, 0.25 to 1%—as can be handled by the metering pump and agitator, and added to the pulp at the maximum dilution possible. Dry polymers require sufficient aging time after initial mixing with water in order to develop their full effectiveness. Liquid polymers—emulsions and dispersions—contain additives such as carriers, activators, and other components which can have an effect on the process and other equipment, and this should be investigated before their use. Care should be taken that the water employed for dissolving as well as for dilution will not affect reagent activity, as this could increase consumption. Prior to design of the system, laboratory tests should be conducted with both plant and tap water to determine if there is a detrimental effect using process water.

Torque Requirements Sufficient torque must be available in the raking mechanism of a full-scale thickener to allow it to move through the slurry and assist solids movement to the underflow outlet. Granular, particulate solids that settle rapidly and reach a terminal solids concentration without going through any apparent compression or zone-settling region require a maximum raking capability, as they must be moved to the outlet solely by the mechanism. At the other end of the spectrum, extremely fine materials, such as clays and precipitates, require a minimum of raking, for most of the solids may reach the underflow outlet hydrodynamically. The rakes prevent a gradual buildup of some solids on the bottom, however, and the gentle stirring action from the rake arm often aids the thickening process. As the underflow concentration approaches its ultimate limit, the consistency will increase greatly, resulting in a higher raking requirement and an increase in torque.

For most materials, the particle size lies somewhere between these two extremes, and the torques required in two properly designed thickeners of the same size but in distinct applications can differ greatly. Unfortunately, test methods to specify torque from small-scale tests are of questionable value, since it is difficult to duplicate actual conditions. Manufacturers of sedimentation equipment select torque ratings from experience with similar substances and will recommend a torque capability on this basis. Definitions of *operating torque* vary with the manufacturer, and the user should ask the supplier to specify the *B-10 life* for bearings and to reference appropriate mechanical standards for continuous operation of the selected gear set at specific torque levels. This will provide guidelines for plant operators and help avoid premature failure of the mechanism. Abnormal conditions above the normal operating torque are inevitable, and a thickener should be provided with sufficient torque capability for short-term operation at higher levels in order to ensure continuous performance.

Underflow Pump Requirements Many suspensions will thicken to a concentration higher than that which can be handled by conventional slurry pumps. Thickening tests should be performed with this in mind, for, in general, the unit area to produce the maximum concentration that can be pumped is the usual design basis. Determination of this ultimate pumpable concentration is largely a judgmental decision requiring some experience with slurry pumping; however, the behavior of the thickened suspension can be used as an approximate guide to pumpability. The supernatant should be decanted following a test and the settled solids repulped in the cylinder to a uniform consistency. Repulping is done easily with a rubber stopper fastened to the end of a rigid rod. If the bulk of the repulped slurry can be poured from the cylinder when it is tilted 10 to 30° above the horizontal, the corresponding thickener underflow can be handled by most types of slurry pumps. But if the slurry requires cylinder shaking or other mechanical means for its removal, it should be diluted to a more fluid condition, if conventional pump systems are to be employed.

THICKENERS

The primary function of a continuous thickener is to concentrate suspended solids by gravity settling so that a steady-state material balance is achieved, solids being withdrawn continuously in the underflow at the rate they are supplied in the feed. Normally, an inventory of pulp is maintained in order to achieve the desired concentration. This volume will vary somewhat as operating conditions change; on occasion, this inventory can be used for storage of solids when feed and underflow rates are reduced or temporarily suspended.

A thickener has several basic components: a tank to contain the slurry, feed piping and a feedwell to allow the feed stream to enter the tank, a rake mechanism to assist in moving the concentrated solids to the withdrawal points, an underflow solids-withdrawal system, and an overflow launder. The basic design of a bridge-supported thickener mechanism is illustrated in Fig. 18-86.

High-Rate Thickeners Flocculants are commonly used in thickeners, and this practice has resulted in thickener classification as either *conventional* or *high-rate*. These designations can be confusing in that they imply that there is a sharp distinction between the two, which *is not* the case. The greater capacity expected from a high-rate thickener is due solely to the effective use of flocculant to maximize throughput, as shown in Fig. 18-87. In most applications, there is a threshold dosage at which a noticeable increase in capacity begins to occur. This effect will continue up to a limit, at which point the capacity will be a maximum unless a lower underflow concentration is accepted, as illustrated in Fig. 18-84. Since flocculant is usually added to a thickener either in the feed line or the feedwell, there are a number of proprietary feedwell designs which are used in high-rate thickeners in order to help optimize flocculation. De-aeration systems may be included in some cases to avoid air entrainment in the flocculated slurry. The other components of these units are not materially different from those of a conventional thickener.

High-Density Thickeners Thickeners can be designed to produce underflows having a very high apparent viscosity, permitting disposal of waste slurries at a concentration that avoids segregation of fines and coarse particles or formation of a free-liquid pond on the surface of the deposit. This practice is applied in *dry-stacking* systems and underground *paste-fill* operations for disposal of mine tailings and similar materials. The thickener mechanism generally will require a special

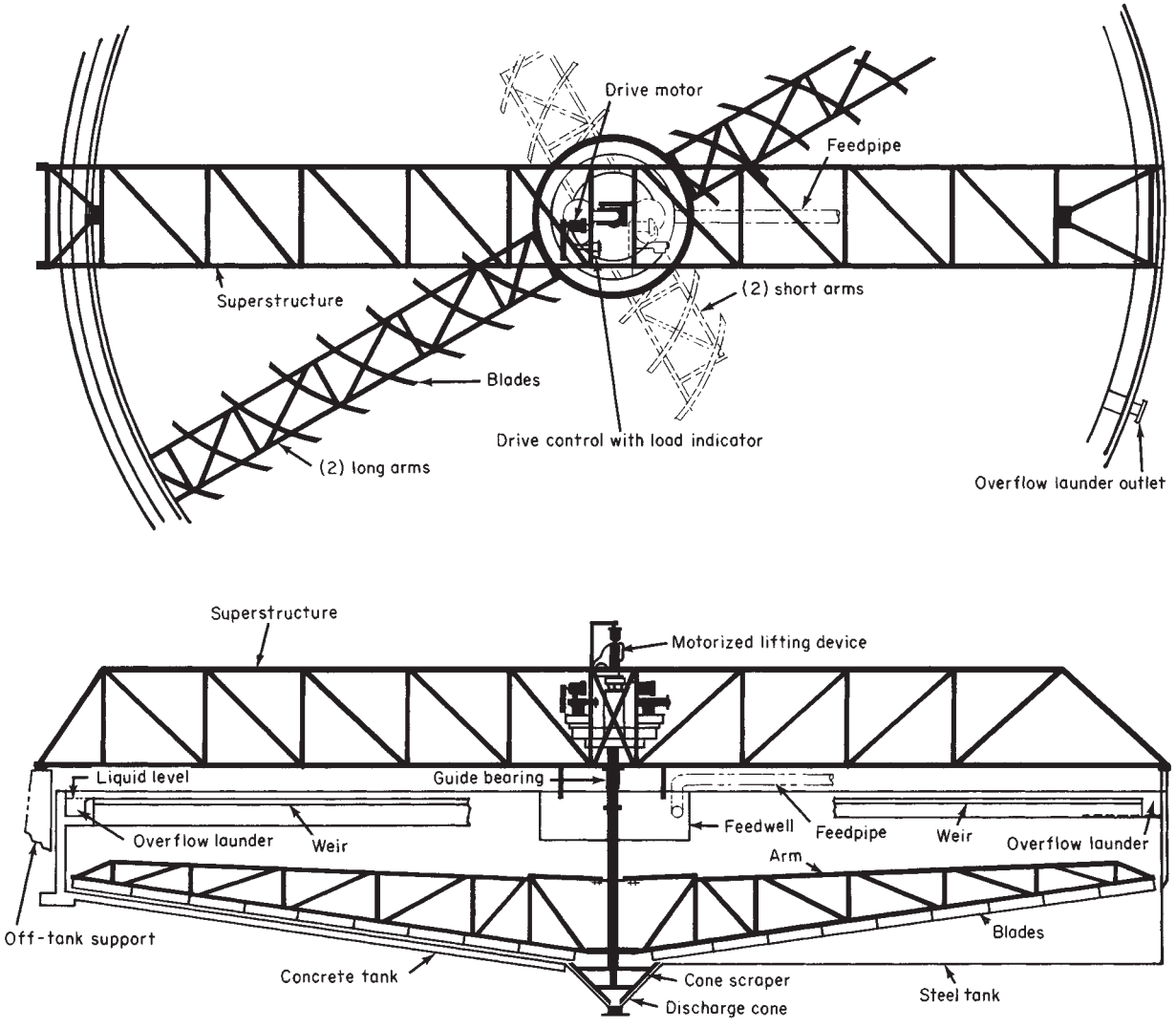


FIG. 18-86 Unit thickener with bridge-supported mechanism. (*EIMCO Process Equipment Co.*)

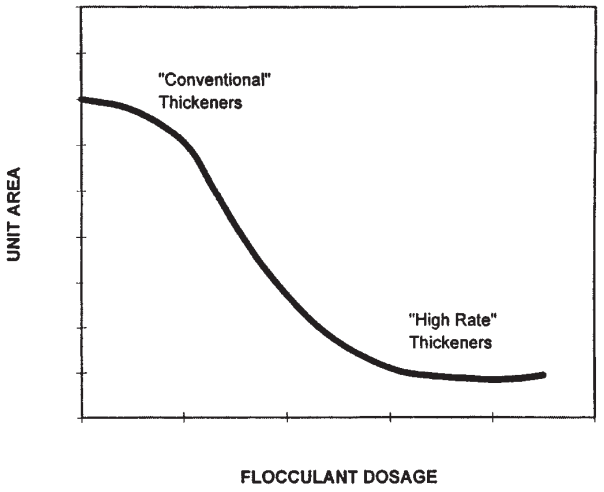


FIG. 18-87 Unit area vs. flocculant dose, illustrating the relationship between conventional and high-rate thickeners.

rake design and have a torque capability 3 to 4 times, or more, the normal for that particular diameter. Underflow slurries usually will be at a solids concentration 5 to 10% lower than that of a vacuum filter cake formed from the same material. Special pumping requirements are necessary if the slurry is to be transferred a significant distance, with line pressure drop typically in the range of 3 to 4 kPa/m of pipeline.

Design Features There are three classes of thickeners, each differentiated by its drive mechanism: (1) bridge-supported, (2) center-column supported, and (3) traction drives. The diameter of the tank will range from 2 to 150 m (6.5 to 492 ft), and the support structure often is related to the size required. These classes are described in detail in the subsection "Components and Accessories for Sedimentation Units."

Operation When operated correctly, thickeners require a minimum of attention and, if the feed characteristics do not change radically, can be expected to maintain design performance consistently. In this regard, it is usually desirable to monitor feed and underflow rates and solids concentrations, flocculant dosage rate, and pulp interface level, preferably with dependable instrumentation systems. Process variations are then easily handled by changing the principal operating controls—underflow rate and flocculant dose—to maintain stability.

Starting up a thickener is usually the most difficult part of the operation, and there is more potential for mechanical damage to the mechanism at this stage than at any other time. In general, two conditions require special attention at this point: underflow pumping and mechanism torque. If possible, the underflow pump should be in operation as soon as feed enters the system, recirculating underflow slurry at a reduced rate if the material is relatively fine or advancing it to the next process step (or disposal) if the feed contains a considerable quantity of coarse solids, e.g., more than 20 percent + 75 μm particles. At this stage of the operation, coarse solids separate from the pulp and produce a difficult raking and pumping situation. Torque can rise rapidly if this material accumulates faster than it is removed. If the torque reaches a point where the automatic control system raises the rakes, it is usually preferable to reduce or cut off the feed completely until the torque drops and the rakes are returned to the lowest position. As the fine fraction of the feed slurry begins to thicken and accumulate in the basin, providing both buoyancy and fluidity, torque will drop and normal feeding can be continued. This applies whether the thickener tank is empty at start-up or filled with liquid. The latter approach contributes to coarse-solids raking problems but at the same time provides conditions more suited to good flocculation, with the result that the thickener will reach stable operation much sooner.

As the solids inventory in the thickener reaches a normal level—usually about 0.5 to 1.0 m below the feedwell outlet—with underflow slurry at the desired concentration, the torque will reach a normal operating range. Special note should be made of the torque reading at this time. Subsequent higher torque levels while operating conditions remain unchanged can almost always be attributed to island formation, and corrective action can be taken early, before serious problems develop. *Island* is the name given to a mass of semisolidified solids that have accumulated on or in front of the rakes, often as a result of excessive flocculant use. This mass usually will continue to grow in size, eventually producing a torque spike that can shut down the thickener and often resulting in lower underflow densities than would otherwise be achievable.

An island is easily detected, usually by the higher-than-normal, gradually increasing torque reading. Probing the rake arms near the thickener center with a rigid rod will confirm this condition—the mass is easily distinguished by its cohesive, claylike consistency. At an early stage, the island is readily removed by raising the rakes until the torque drops to a minimum value. The rakes are then lowered gradually, a few centimeters at a time, so as to shave off the mass of solids and discharge this gelled material through the underflow. This operation can take several hours, and if island formation is a frequent occurrence, the procedure should be carried out on a regular basis, typically once a day, preferably with an automatic system to control the entire operation.

Stable thickener performance can be maintained by carefully monitoring operating conditions, particularly the pulp interface level and the underflow rate and concentration. As process changes occur, the pulp level can vary; regulation of the underflow pumping rate will keep the level within the desired range. If the underflow varies in concentration, this can be corrected by adjusting the flocculant dosage. Response will not be immediate, of course, and care should be taken to make only small step changes at any one time. Procedures for use of automatic control are described in the section on instrumentation.

CLARIFIERS

Continuous clarifiers generally are employed with dilute suspensions, principally industrial process streams and domestic municipal wastes, and their primary purpose is to produce a relatively clear overflow. They are basically identical to thickeners in design and layout except that they employ a mechanism of lighter construction and a drive head with a lower torque capability. These differences are permitted in clarification applications because the thickened pulp produced is smaller in volume and appreciably lower in suspended solids concentration, owing in part to the large percentage of relatively fine (smaller than 10 μm) solids. The installed cost of a clarifier, therefore, is approximately 5 to 10 percent less than that of a thickener of equal tank size, as given in Fig. 18-94.

Rectangular Clarifiers Rectangular clarifiers are employed primarily in municipal water and waste treatment plants, as well as in certain industrial plants, also for waste streams. The raking mechanism employed in many designs consists of a chaintype drag, although suction systems are used for light-duty applications. The drag moves the deposited pulp to a sludge hopper located on one end by means of scrapers fixed to endless chains. During their return to the sludge raking position, the flights may travel near the water level and thus act as skimming devices for removal of surface scum. Rectangular clarifiers are available in widths of 2 to 10 m (6 to 33 ft). The length is generally 3 to 5 times the width. The larger widths have multiple raking mechanisms, each with a separate drive.

This type of clarifier is used in applications such as preliminary oil-water separations in refineries and clarification of waste streams in steel mills. When multiple units are employed, common walls are possible, reducing construction costs and saving on floor space. Overflow clarities, however, generally are not as good as with circular clarifiers, due primarily to reduced overflow weir length for equivalent areas.

Circular Clarifiers Circular units are available in the same three basic types as single-compartment thickeners: bridge, center-column, and peripheral-traction. Because of economic considerations, the bridge-supported type is limited generally to tanks less than 20 m in diameter.

A circular clarifier often is equipped with a surface-skimming device, which includes a rotating skimmer, scum baffle, and scum-box assembly. In sewage and organic-waste applications, squeegees normally are provided for the rake-arm blades, as it is desirable that the bottom be scraped clean to preclude accumulation of organic solids, with resultant septicity and flotation of decomposing material.

Center-drive mechanisms are also installed in square tanks. This mechanism differs from the standard circular mechanism in that a hinged corner blade is provided to sweep the corners which lie outside the path of the main mechanism.

Clarifier-Thickener Clarifiers can serve as thickeners, achieving additional densification in a deep sludge sump adjacent to the center that extends a short distance radially and provides adequate retention time and pulp depth to compact the solids to a high density. Drive mechanisms on this type of clarifier usually must have higher torque capability than would be supplied on a standard clarifier.

Industrial Waste Secondary Clarifiers Many plants which formerly discharged organic wastes to the sewer have turned to using their own treatment facilities in order to reduce municipal treatment plant charges. For organic wastes, the waste-activated sludge process is a preferred approach, using an aeration basin for the bio-oxidation step and a secondary clarifier to produce a clear effluent and to concentrate the biomass for recycling to the basin. To produce an acceptable effluent and achieve sufficient concentration of the low-density solids that make up the biomass, certain design criteria must be followed. If pilot-plant data are unavailable, the design procedures proposed by Albertson (op. cit.) can be used to specify tank diameter, depth, feedwell dimensions, feed inlet configuration, and rake-blade design for a unit which will meet the specifications for many waste-activated sludge plants. Typical design parameters recommended by Albertson include the following:

Feed pipe velocity: ≤1.2 m/s.

Energy-dissipating feed entry velocity (tangential): ≤0.5 m/s.

Downward velocity from feedwell: ≤0.5–0.75 (peak) m/min.

Feedwell depth: Entry port depth +1 m.

Radial velocity below feedwell: ≤90% of downward velocity.

Tank depth: Clear water zone above dense sludge blanket is determined largely by clarification requirements; typically 3–5 m.

Tank diameter: Largely a function of clear water depth; the maximum overflow rate in m/h = 0.278 × clear water depth. Resulting underflow design settling velocity should be less than 1.0 m/h for 1% solids and 120 mL/g SVI.

Tilted-Plate Clarifiers Lamella or tilted-plate separators have achieved increased use for clarification. They contain a multiplicity of plates inclined at 45 to 60° from the horizontal. Various feed methods are employed so that the influent passes into each inclined channel at about one-third of the vertical height from the bottom. This results in the solids having to settle only a short distance in each channel before sliding down the base to the collection zone beneath the plates. The clarified liquid passes in the opposite direction beneath the ceiling of each channel to the overflow connection.

The area that is theoretically available for separation is equal to the sum of the projected areas or all channels on the horizontal plane. Figure 18-88 shows the horizontally projected area A, of a single channel in a clarifier of unit width. If X is the uniform distance between plates (measured perpendicularly to the plate surface), the clarifier will contain $\sin \alpha/X$ channels per unit length and an effective collection area per unit clarifier length of A, $\sin \alpha/X$, where α is the angle of inclination of the plates to the horizontal. It follows that the total horizontally projected plate area per unit volume of sludge in the clarifier A_s is

$$A_s = \cos \alpha/X \qquad (18\text{-}48)$$

As α and X are decreased, A_s is increased. However, α must be larger than the angle of repose of the sludge so that it will slide down the plate, and the most common range is 55 to 60°. Plate spacing must be large enough to accommodate the opposite flows of liquid and sludge while reducing interference and preventing plugging and to provide enough residence time for the solids to settle to the bottom plate. Usual X values are 50 to 75 mm (2 to 3 in).

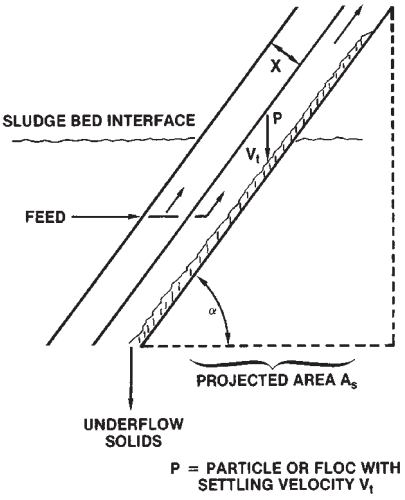


FIG. 18-88 Basic concept of the Lamella-type clarifier.

Many different designs are available, the major difference among them being in feed-distribution methods and plate configurations. Operating capacities range from 1 to 3 m^3 of feed/h/m^2 of projected horizontal area [0.4 to 1.2 gal/(min·ft)].

The principal advantage of the tilted-plate clarifier is the increased capacity per unit of plane area. Major disadvantages are an underflow solids concentration that generally is lower than in other gravity clarifiers and difficulty of cleaning when scaling or deposition occurs. The lower underflow composition is due primarily to the reduced compression-zone volume relative to the large settling area. When flocculants are employed, flocculating equipment and tankage preceding the separator are required, as the design does not permit internal flocculation.

Solids-Contact Clarifiers When desirable, mixing, flocculation, and sedimentation all may be accomplished in a single tank. Of the various designs available, those employing mechanically assisted mixing in the reaction zone are the most efficient. They generally permit the highest overflow rate at a minimum chemical dosage while producing the best effluent quality. The unit illustrated in Fig. 18-89 consists of a combination dual drive which moves the rake mechanism at a very slow speed as it rotates a high-pumping-rate, low-shear turbine located in the top portion of a center reaction well at a very much higher speed. The influent, dosed with chemicals as it enters, is contacted with previously settled solids in a recirculation draft tube within the reaction well by means of the pumping action of the turbine, resulting in a thorough mixing of these streams. Owing to the higher concentration of solids being recirculated, all chemical reactions are more rapid and more nearly complete, and flocculation is improved. The mixture passes out of the contacting and reaction well into the clarification area, where the flocculated particles settle out. They are raked to the center to be used again in the recirculation process, with a small amount being discharged through the sludge pump. When floccules are too heavy to be circulated up through the draft tube (as in the case of metallurgical pulps), a modified design using external recirculation of a portion of the thickened underflow is chosen. These units employ a special mixing impeller in a large feed well with a small-diameter central outlet.

Solids-contact clarifiers are advantageous for clarifying turbid waters or slurries that require coagulation and flocculation for the removal of bacteria, suspended solids, or color. Applications include softening water by lime addition; clarifying industrial-process streams, sewage, and industrial wastewaters; tertiary treatment for removal of phosphates, BOD_5, and turbidity; and silica removal from geothermal brines or from surface water for cooling-tower makeup.

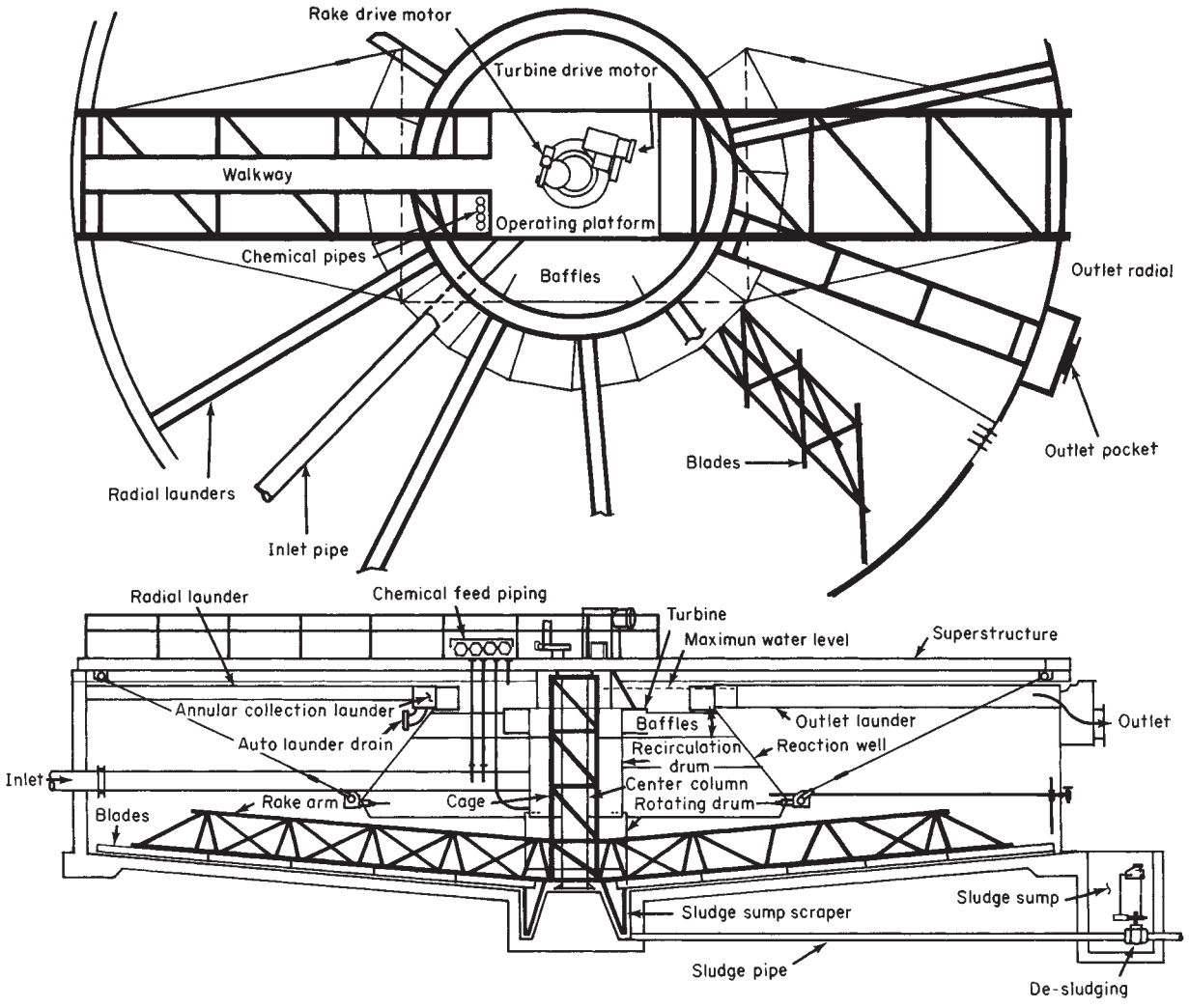


FIG. 18-89 Reactor-clarifier of the high-rate solids-contact type. (*EIMCO Process Equipment Co.*)

COMPONENTS AND ACCESSORIES FOR SEDIMENTATION UNITS

Sedimentation systems consist of a collection of components, each of which can be supplied in a number of variations. The basic components are the same, whether the system is for thickening or clarifying: tank, drive-support structure, drive unit and lifting device, rake structure, feedwell, overflow arrangement, underflow arrangement, instrumentation, and flocculation facilities.

Tanks Tanks or basins are constructed of such materials as steel, concrete, wood, compacted earth, plastic sheeting, and soil cement. The selection of the materials of construction is based on cost, availability, topography, water table, ground conditions, climate, operating temperature, and chemical-corrosion resistance. Typically, industrial tanks up to 30 m (100 ft) in diameter are made of steel. Concrete generally is used in municipal applications and in larger industrial applications. Extremely large units employing earthen basins with impermeable liners have proved to be economical.

Drive-Support Structures There are three basic drive mechanisms. These are (1) the bridge-supported mechanism, (2) the center-column-supported mechanism, and (3) the traction-drive thickener containing a center-column-supported mechanism with the driving arm attached to a motorized carriage at the tank periphery.

Bridge-Supported Thickeners These thickeners (Fig. 18-86) are common in diameters up to 30 m, the maximum being about 45 m (150 ft). They offer the following advantages over a center-column-supported design: (1) ability to transfer loads to the tank periphery; (2) ability to give a denser and more consistent underflow concentration with the single draw-off point; (3) a less complicated lifting device; (4) fewer structural members subject to mud accumulation; (5) access to the drive from both ends of the bridge; and (6) lower cost for units smaller than 30 m in diameter.

Center-Column-Supported Thickeners These thickeners are usually 20 m (65 ft) or more in diameter. The mechanism is supported by a stationary steel or concrete center column, and the raking arms are attached to a driving cage which rotates around the center column.

Traction Thickeners These thickeners are most adaptable to tanks larger than 60 m (200 ft) in diameter. Maintenance generally is less difficult than with other types of thickeners, which is an advantage

in remote locations. The installed cost of the traction thickener may be more than that of a center-driven unit primarily because of the cost of constructing the heavy concrete wall required to support the drive carriage. Disadvantages of the traction thickener are that (1) no practical lifting device can be used, (2) operation may be difficult in climates where snow and ice are common, and (3) the driving-torque effort must be transmitted from the tank periphery to the center, where the heaviest raking conditions occur.

Drive Assemblies The drive assembly is the key component of a sedimentation unit. The drive assembly provides (1) the force to move the rakes through the thickened pulp and to move settled solids to the point of discharge, (2) the support for the mechanism which permits it to rotate, (3) adequate reserve capacity to withstand upsets and temporary overloads, and (4) a reliable control which protects the mechanism from damage when a major overload occurs.

Drives usually have steel or iron main spur gears mounted on bearings, alloy-steel pinions, and either a bronze or a malleable iron worm gear driven by a hardened-steel worm or a planetary gear system. Direct-drive hydraulic systems are also employed. The gearing components preferably are enclosed for maximum service life. The drive typically includes a torque-measuring system with torque indicated on the mechanism and often transmitted to a remote indicator. If the torque becomes excessive, it can automatically activate such safeguards against structural damage as sounding an alarm, raising the rakes, and stopping the drive.

Rake-Lifting Mechanisms These should be provided when abnormal thickener operation is probable. Abnormal thickener operation or excessive torque may result from insufficient underflow pumping, surges in the solids feed rate, excessive amounts of large particles, sloughing of solids accumulated between the rakes and the bottom of the tank or on structural members of the rake mechanism, or miscellaneous obstructions falling into the thickener. The lifting mechanism may be set to raise the rakes automatically when a specific torque level (e.g., 40 percent of design) is encountered, continuing to lift until the torque returns to normal or until the maximum lift height is reached. Generally, corrective action must be taken to eliminate the cause of the upset. Once the torque returns to normal, the rake mechanism is lowered slowly to "plow" gradually through the excess accumulated solids until these are removed from the tank.

Rake-lifting devices can be manual for small-diameter thickeners or motorized for larger ones. Manual rake-lifting devices consist of a handwheel and a worm to raise or lower the rake mechanism by a distance usually ranging from 30 to 60 cm (1 to 2 ft). Motorized rake-lifting devices typically are designed to allow for a vertical lift of the rake mechanism of up to 90 cm (3 ft). A platform-type lifting device lifts the entire drive and rake mechanism up to 2.5 m (8 ft) and is used for applications in which excessive torque is most probable or when storage of solids in the thickener is desired.

Figure 18-90 illustrates the cable-arm design. This design uses cables attached to a truss above or near the liquid surface to move the rake arms, which are hinged to the drive structure, allowing the rakes to be raised when excessive torque is encountered. A major advantage of this design is the relatively small surface area of the raking mechanism, which reduces the solids accumulation and downtime in applications in which scaling or island formation can occur.

One disadvantage of this or any hinged-arm or other self-lifting design is that there is very little lift at the center, where the overload usually occurs. A further disadvantage is the difficulty of returning the rakes to the lowered position in settlers containing solids that compact firmly.

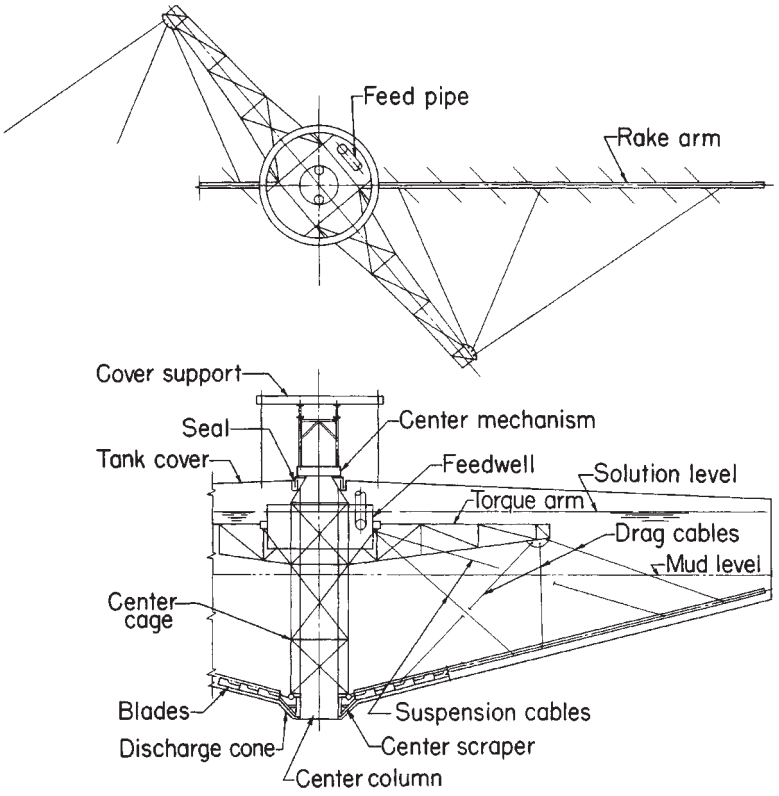


FIG. 18-90 Cable-arm design. (*Dorr-Oliver, Inc.*)

Rake Mechanism The rake mechanism assists in moving the settled solids to the point of discharge. It also aids in thickening the pulp by disrupting bridged floccules, permitting trapped fluid to escape and allowing the floccules to become more consolidated. Rake mechanisms are designed for specific applications, usually having two long rake arms with an option for two short rake arms for bridge-supported and center-column-supported units. Traction units usually have one long arm and three short arms.

Figure 18-91 illustrates three types of rake-arm designs. The conventional design typically is used in bridge-supported units, while the dual-slope design is used for units of larger diameter. The "thixo post" design employs rake blades on vertical posts extending below the truss to keep the truss out of the thickest pulp and thereby prevent the collection of solids that might cause an "island" to form.

Rake blades can have attached spikes or serrated bottoms to cut into solids that have a tendency to compact. Lifting devices typically are used with these applications.

Rake-speed requirements depend on the type of solids entering the thickener. Peripheral speed ranges used are, for slow-settling solids, 3 to 8 m/min (10 to 25 ft/min); for fast-settling solids, 8 to 12 m/min (25 to 40 ft/min); and for coarse solids or crystalline materials, 12 to 30 m/min (40 to 100 ft/min).

Feedwell The feedwell is designed to allow the feed to enter the thickener with minimum turbulence and uniform distribution while dissipating most of its kinetic energy. Feed slurry enters the feedwell, which is usually located in the center of the thickener, through a pipe or launder suspended from the bridge. To avoid excess velocity, an open launder normally has a slope no greater than 1 to 2 percent. Pulp should enter the launder at a velocity that prevents sanding at the inlet. With nonsanding pulps, the feed may also enter upward through the center column from a pipeline installed beneath the tank.

The standard feedwell for a thickener is designed for a maximum vertical outlet velocity of about 1.5 m/min (5 ft/min). High turbidity caused by short-circuiting the feed to the overflow can be reduced by increasing the depth of the feedwell. When overflow clarity is important or the solids specific gravity is close to the liquid specific gravity, deep feedwells of large diameter are used, and measures are taken to reduce the velocity of the entering feed slurry.

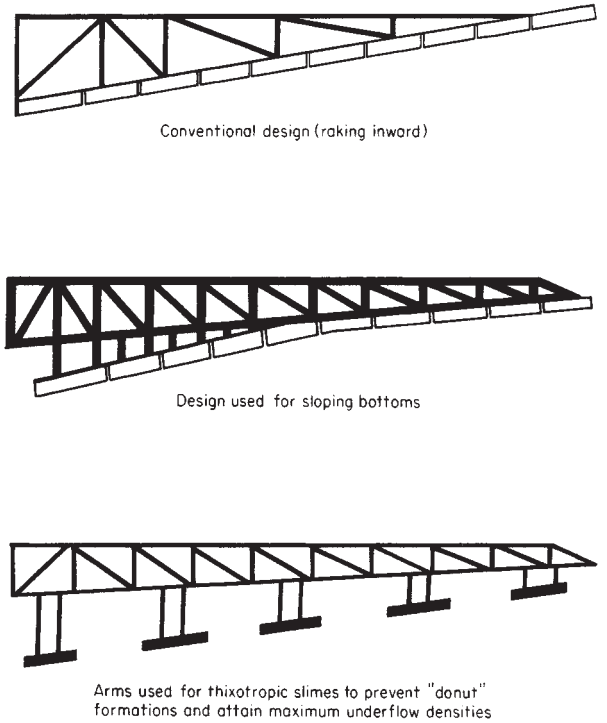


FIG. 18-91 Rake-mechanism designs employed for specific duties. (*EIMCO Process Equipment Co.*)

Shallow feedwells may be used when overflow clarity is not important, the overflow rate is low, and/or solids density is appreciably greater than that of water. Some special feedwell designs used to dissipate entrance velocity and create quiescent settling conditions split the feed stream and allow it to enter the feedwell tangentially on opposite sides. The two streams shear or collide with one another to dissipate kinetic energy.

When flocculants are used, often it will be found that the optimum solids concentration for flocculation is considerably less than the normal concentration, and significant savings in reagent cost will be made possible by dilution of the feed prior to flocculation. This can be achieved by recycling overflow or more efficiently by feedwell modifications, including openings in the feedwell rim. These will allow supernatant to enter the feedwell, and flocculant can be added at this point or injected below the surface of the pulp in the feedwell. Another effective means of achieving this dilution prior to flocculant addition is illustrated in Fig. 18-92. This approach utilizes the energy available in the incoming feed stream to achieve the dilution by momentum transfer and requires no additional energy expenditure to dilute this slurry by as much as three to four times.

Overflow Arrangements Clarified effluent typically is removed in a peripheral launder located inside or outside the tank. The effluent enters the launder by overflowing a V-notch or level flat weir, or through submerged orifices in the bottom of the launder. Uneven overflow rates caused by wind blowing across the liquid surface in large thickeners can be better controlled when submerged orifices or V-notch weirs are used. Radial launders are used when uniform upward liquid flow is desired in order to improve clarifier detention efficiency. This arrangement provides an additional benefit in reducing the effect of wind, which can seriously impair clarity in applications that employ basins of large diameter.

The hydraulic capacity of a launder must be sufficient to prevent flooding, which can cause short-circuiting of the feed and deterioration of overflow clarity. Standards are occasionally imposed on weir overflow rates for clarifiers used in municipal applications; typical rates are 3.5 to 15 $m^3/(h \cdot m)$ [7000 to 30,000 gal/(day·ft)], and they are highly dependent on clarifier side-water depth. Industrial clarifiers may have higher overflow rates, depending on the application and the desired overflow clarity. Launders can be arranged in a variety of configurations to achieve the desired overflow rate. Several alternatives to improve clarity include an annular launder inside the tank (the liquid overflows both sides), radial launders connected to the peripheral launder (providing the very long weir that may be needed when abnormally high overflow rates are encountered and overflow clarity is important), and Stamford baffles, which are located below the launder to direct flow currents back toward the center of the clarifier.

In many thickener applications, on the other hand, complete peripheral launders are not required, and no difference in either overflow clarity or underflow concentration will result through the use of launders extending over only a fraction (e.g., one-fifth) of the perimeter. For design purposes, a weir-loading rate in the range of 7.5 to 30.0 $m^3/(h \cdot m)$ [10 to 40 gpm/ft] can be used, the higher values being employed with well-flocculated, rapidly settling slurries. The overflow launder required may occupy only a single section of the perimeter rather than consisting of multiple, shorter segments spaced uniformly around the tank.

Underflow Arrangements Concentrated solids are removed from the thickener by use of centrifugal or positive displacement pumps or, particularly with large-volume flows, by gravity discharge through a flow control valve or orifice suitable for slurry applications. Due to the risk to the thickener operation of a plugged underflow pipe, it is recommended that duplicate underflow pipes and pumps be installed in all thickening applications. Provision to recycle underflow slurry back to the feedwell is also useful, particularly if solids are to be stored in the thickener.



FIG. 18-92 E-Duc® Feed dilution system installed on 122-m-diameter thickener. (*EIMCO Process Equipment Co.*)

There are several basic underflow arrangements: (1) the underflow pump adjacent to the thickener sidewall with buried piping from the discharge cone, (2) the underflow pump under the thickeners or adjacent to the sidewall with the piping from the discharge cone in a tunnel, (3) the underflow pump adjacent to the thickener sidewall with a peripheral discharge from the tank sidewall, and (4) the underflow pump located in the center of the thickener on the bridge close to the drive mechanism, or at the perimeter, using piping up through the center column.

Pump Adjacent to Thickener with Buried Piping This arrangement of buried piping from the discharge cone is the least expensive system but the most susceptible to plugging. It is used only when the solids do not compact to an unpumpable slurry and can be easily backflushed if plugging occurs. Typically, two or more underflow pipes are installed from the discharge cone to the underflow pump so that solids removal can continue if one of the lines plugs. Valves should be installed to permit flushing with water and compressed air in both directions to remove blockages.

Tunnel A tunnel may be constructed under the thickener to provide access to the discharge cone when underflow slurries are difficult to pump and have characteristics that cause plugging. The underflow pump may be installed underneath the thickener or at the perimeter. Occasionally thickeners are installed on legs or piers, making tunneling for access to the center unnecessary. A tunnel or an elevated thickener is more expensive than the other underflow arrangements, but there are certain operational and maintenance advantages. Of course, the hazards of working in a tunnel (flooding and interrupted ventilation, for example) and related safety regulations must be considered.

Peripheral Discharge Peripheral discharge sometimes is used to permit the reduced installation cost of a flat-bottom tank on compacted soil. Because more torque is required to rake the solids to the perimeter of the tank, this arrangement is not suitable for service involving coarse solids or solids that become nonfluid at high concentrations.

Center-Column Pumping This arrangement may be used instead of a tunnel. Several designs are available. The commonest is a bridge-mounted pump with a suction line through a wet or dry center column. The pump selection may be limiting, requiring special attention to priming, net positive suction head, and the maximum density that the pump can handle. One design has the underflow pump located in a room under the thickener mechanism and connected to openings in the column. Access is through the drive gear at the top of the column.

INSTRUMENTATION

Thickener control philosophies are usually based on the idea that the underflow density obtained is the most important performance criterion. The overflow clarity is also a consideration, but this is generally not as critical. Additional factors which must be considered are optimization of flocculant usage and protection of the raking mechanism.

Automated control schemes employ one or more sets of controls, which will fit into three categories: (1) control loops which are used to regulate the addition of flocculant, (2) control loops to regulate the withdrawal of underflow, and (3) rake drive controls. Usually, the feed to a thickener is not controlled and most control systems have been designed with some flexibility to deal with changes in feed characteristics, such as an increase in volume or alteration in the nature of the solids themselves. In severe cases, some equalization of the feed is required in order to allow the control system to perform effectively.

Flocculant addition rate can be regulated in proportion to the thickener volumetric feed rate or solids mass flow in a feed-forward mode, or in a feed-back mode on either rake torque, underflow density, settling solids (sludge) bed level, or solids settling rate. Of these, feed-forward on mass flow or feed-back on bed level are probably the most common. In some feed-forward schemes, the ratio multiplier is trimmed by one of the other parameters.

Underflow is usually withdrawn continuously on the bases of bed level, rake torque, or underflow solids concentration in a feed-back mode. Most installations incorporate at least two of these parameters in their underflow withdrawal control philosophy. For example, the continuous withdrawal may be based on underflow solids density with an override to increase the withdrawal rate if either the rake torque or the bed level reaches a preset value. In some cases, underflow withdrawal has been regulated in a feed-forward mode on the basis of thickener feed solids mass flow rate. Any automated underflow pumping scheme should incorporate a lower limit on volumetric flow rate as a safeguard against line pluggage.

It is also important to consider the level of the sludge bed in the thickener. Although this can be allowed to increase or decrease within moderate limits, it must be controlled enough to prevent solids from overflowing the thickener or from falling so low that the underflow density becomes too dilute. The settling slurry within the sludge bed is normally free flowing and will disperse to a consistent level across the thickener diameter.

Rake drive controls protect the drive mechanism from damage and usually incorporate an alarm to indicate high torque with an interlock to shut down the drive at a higher torque level. They can have an automated rake raising and lowering feature with a device to indicate the elevation of the rakes.

A complete automated control scheme incorporates controls from each of the three categories. It is important to consider the interaction of the various controls, especially of the flocculant addition and underflow withdrawal control loops, when designing a system. The lag and dead times of any feedback loops as well as the actual response of the system to changes in manipulated variables must be considered. For example, in some applications it is possible that excessive flocculant addition may produce an increase in the rake torque (due to island formation or viscosity increase) without a corresponding increase in underflow density. Additionally, sludge bed level sensors generally require periodic cleaning to produce a reliable signal. In many cases, it has not been possible to effectively maintain the sludge bed level sensors, requiring a change in the thickener control logic after start-up. Some manufacturers offer complete thickener control packages.

Control philosophies for clarifiers are based on the idea that the overflow is the most important performance criterion. Underflow density or suspended solids content is a consideration, as is optimal use of flocculation and pH control reagents. Automated controls are of three basic types: (1) control loops that optimize coagulant, flocculant, and pH control reagent additions; (2) those that regulate underflow removal; and (3) rake drive controls. Equalization of the feed is provided in some installations, but the clarifier feed is usually not a controlled variable with respect to the clarifier operation.

Automated controls for flocculating reagents can use a feed-forward mode based on feed turbidity and feed volumetric rate, or a feed-back mode incorporating a streaming current detector on the flocculated feed. Attempts to control coagulant addition on the basis of overflow turbidity generally have been less successful. Control for pH has been accomplished by feed-forward modes on the feed pH and by feed-back modes on the basis of clarifier feedwell or external reaction tank pH. Control loops based on measurement of feedwell pH are useful for control in applications in which flocculated solids are internally recirculated within the clarifier feedwell.

Automated sludge withdrawal controls are usually based on the sludge bed level. These can operate in on-off or continuous modes and will use either single-point or continuous sludge level indication sensors. In many applications, automated control of underflow withdrawal does not provide an advantage, since so few settled solids are produced that it is only necessary to remove sludge for a short interval once a day, or even less frequently. In applications in which the underflow is recirculated internally within the feedwell, it is necessary to maintain sufficient sludge inventory for the recirculation turbine to pull from. This could be handled in an automated system with a single-point *low* sludge bed level sensor in conjunction with a low-level alarm or pump shutoff solenoid. Some applications require continuous external recirculation of the underflow direct to the feedwell or external reaction tanks, and an automated control loop could be used to maintain recirculation based on flow measurement, with a manually adjusted setpoint.

Control philosophies applied to continuous countercurrent decantation (CCD) thickeners are similar to those used for thickeners in other applications, but have emphasis on maintaining the CCD circuit in balance. It is important to prevent any one of the thickeners from pumping out too fast, otherwise an upstream unit could be starved of wash liquor while at the same too much underflow could be placed in a downstream unit too quickly, disrupting the operation of both units as well as reducing the circuit washing efficiency. Several control configurations have been attempted, and the more successful schemes have linked the solids mass flow rate of underflow pumping to that of the upstream unit or to the CCD circuit solids mass feed rate. Wide variations in the solids feed rate to a CCD circuit will require some means of dampening these fluctuations if design wash efficiency is to be maintained.

The following types of devices are commonly applied to measure the various operational parameters of thickeners and clarifiers. They have been used in conjunction with automatic valves and variable-speed pumps to achieve automatic operation as well as to simply provide local or remote indications.

Sludge Bed Level Sensors Most of the more commonly used devices for detection of the sludge bed level operate on principles of ultrasound, gamma radiation, infrared or visible light, or simply with a float that is carefully weighted to float on the sludge bed level interface. There are basically two types of sensors, those that provide a single-point indication at a fixed height within the thickener or clarifier, and those that follow the sludge bed depth over a distance and provide a continuous indication of the level. Some devices are available that can provide a profile of the slurry concentration within the sludge bed.

Flowmeters These are used to measure flocculant addition, underflow, and feed flow rates. For automatic control, the more commonly used devices are magnetic flowmeters and Doppler effect flowmeters.

Density Gauges These are used to measure the density or suspended solids content of the feed and underflow streams. Gamma radiation devices are the most commonly used for automatic control, but ultrasonic devices are effective in the lower range of slurry density. Marcy pulp density scales are an effective manually operated device. A solids "mass flow" indication is usually obtained by combining a density gauge output with the output from a flowmeter.

Turbidity Gauges These operate with visible light beams and detectors. They are used to monitor feed and effluent turbidity.

Streaming Current Detectors These units produce a measurement closely related to the zeta potential of a suspension and are used successfully in optimizing the coagulant dose in clarification applications.

CONTINUOUS COUNTERCURRENT DECANTATION

The system of separation of solid-phase material from an associated solution by repeated stages of dilution and gravity sedimentation is adapted for many industrial-processing applications through an operation known as continuous countercurrent decantation (CCD). The flow of solids proceeds in a direction countercurrent to the flow of solution diluent (water, usually), with each stage composed of a mixing step followed by settling of the solids from the suspension. The number of stages ranges from 2 to as many as 10, depending on the degree of separation required, the amount of wash fluid added (which influences the final solute concentration in the first-stage overflow), and the underflow solids concentration attainable. Applications include processes in which the solution is the valuable component (as in alumina extraction), or in which purified solids are sought (magnesium hydroxide from seawater), or both (as frequently encountered in the chemical-processing industry and in base-metal hydrometallurgy).

The factors which may make CCD a preferred choice over other separation systems include the following: rapidly settling solids, assisted by flocculation: relatively high ratio of solids concentration between underflow and feed; moderately high wash ratios allowable (2 to 4 times the volume of liquor in the thickened underflows); large quantity of solids to be processed; and the presence of fine-size solids that are difficult to concentrate by other means. A technical feasibility and economic study is desirable in order to make the optimum choice.

Flow-Sheet Design Thickener-sizing tests, as described earlier, will determine unit areas, flocculant dosages, and underflow densities for the various stages. For most cases, unit areas will not vary significantly throughout the circuit; similarly, underflow concentrations should be relatively constant. In practice, the same unit area is generally used for all thickeners in the circuit to simplify construction.

Equipment The equipment selected for CCD circuits may consist of multiple-compartment washing-tray thickeners or a train of

individual unit thickeners. The washing-tray thickener consists of a vertical array of coaxial trays connected in series, contained in a single tank. The advantages of this design are smaller floor-area requirements, less pumping equipment and piping, and reduced heat losses in circuits operating at elevated temperatures. However, operation is generally more difficult and user preference has shifted toward unit thickeners despite the larger floor-area requirement and greater initial cost.

Underflow Pumping Diaphragm pumps with open discharge are employed in some cases, primarily because underflow densities are readily controlled with these units. Disadvantages include the generally higher maintenance and initial costs than for other types and their inability to transfer the slurry any great distance. Large flows often are best handled with variable-speed, rubber-lined centrifugal pumps, utilizing automatic control to maintain the underflow rate and density.

Overflow Pumps These can be omitted if the thickeners are located at increasing elevations from first to last so that overflows are transferred by gravity or if the mixture of underflow and overflow is to be pumped. Overflow pumps are necessary, however, when maximum flexibility and control are sought.

Interstage Mixing Efficiencies Mixing or stage efficiencies rarely achieve the ideal 100 percent, in which solute concentrations in overflow and underflow liquor from each thickener are identical. Part of the deficiency is due to insufficient blending of the two streams, and attaining equilibrium will be hampered further by heavily flocculated solids. In systems in which flocculants are used, interstage effi-

TABLE 18-7 Typical Thickener and Clarifier Design Criteria and Operating Conditions

	Percent solids		Unit area, $m^2/(t/d)$*†	Overflow rate, $m^3/(m^2 \cdot h)$*
	Feed	Underflow		
Alumina Bayer process				
Red mud, primary	3–4	10–25	2–5	
Red mud, washers	6–8	15–35	1–4	
Hydrate, fine or seed	1–10	20–50	1.2–3	0.07–0.12
Brine purification	0.2–2.0	8–15		0.5–1.2
Coal, refuse	0.5–6	20–40	0.5–1	0.7–1.7
Coal, heavy-media (magnetic)	20–30	60–70	0.05–0.1	
Cyanide, leached-ore	16–33	40–60	0.3–1.3	
Flue dust, blast-furnace	0.2–2.0	40–60		1.5–3.7
Flue dust, BOF	0.2–2.0	30–70		1–3.7
Flue-gas desulfurization sludge	3–12	20–45	0.3–3†	
Magnesium hydroxide from brine	8–10	25–40	5–10	
Magnesium hydroxide from seawater	1–4	15–20	3–10	0.5–0.8
Metallurgical				
Copper concentrates	14–50	40–75	0.2–2	
Copper tailings	10–30	45–65	0.4–1	
Iron ore				
Concentrate (magnetic)	20–35	50–70	0.01–0.08	
Concentrate (nonmagnetic), coarse: 40–65% –325	25–40	60–75	0.02–0.1	
Concentrate (nonmagnetic), fine: 65–100% –325	15–30	60–70	0.15–0.4	
Tailings (magnetic)	2–5	45–60	0.6–1.5	1.2–2.4
Tailings (nonmagnetic)	2–10	45–50	0.8–3	0.7–1.2
Lead concentrates	20–25	60–80	0.5–1	
Molybdenum concentrates	10–35	50–60	0.2–0.4	
Nickel, $(NH_4)_2CO_3$ leach residue	15–25	45–60	0.3–0.5	
Nickel, acid leach residue	20	60	0.8	
Zinc concentrates	10–20	50–60	0.3–0.7	
Zinc leach residue	5–10	25–40	0.8–1.5	
Municipal waste				
Primary clarifier	0.02–0.05	0.5–1.5		1–1.7
Thickening				
Primary sludge	1–3	5–10	8	
Waste-activated sludge	0.2–1.5	2–3	33	
Anaerobically digested sludge	4–8	6–12	10	
Phosphate slimes	1–3	5–15	1.2–18	
Pickle liquor and rinse water	1–8	9–18	3.5–5	
Plating waste	2–5	5–30		1.2
Potash slimes	1–5	6–25	4–12	
Potato-processing waste	0.3–0.5	5–6		1
Pulp and paper				
Green-liquor clarifier	0.2	5		0.8
White-liquor clarifier	8	35–45	0.8–1.6	
Kraft waste	0.01–0.05	2–5		0.8–1.2
Deinking waste	0.01–0.05	4–7		1–1.2
Paper-mill waste	0.01–0.05	2–8		1.2–2.2
Sugarcane defecation			0.5‡	
Sugar-beet carbonation	2–5	15–20	0.03–0.07‡	
Uranium				
Acid-leached ore	10–30	25–65	0.02–1	
Alkaline-leached ore	20	60	1	
Uranium precipitate	1–2	10–25	5–12.5	
Water treatment				
Clarification (after 30-min flocculation)				1–1.3
Softening lime-soda (high-rate, solids-contact clarifiers)				3.7
Softening lime-sludge	5–10	20–45	0.6–2.5	

*$m^2/(t/d) \times 9.76 = ft^2/(short\ ton/day)$; $m^3/(m^2 \cdot h) \times 0.41 = gal/(ft^2 \cdot min)$; 1 t = 1 metric ton.
†High-rate thickeners using required flocculant dosages operate at 10 to 50 percent of these unit areas.
‡Basis: 1 t of cane or beets.

ciencies often will drop gradually from first to last thickener, and typical values will range from 98 percent to as low as 70 percent. In some cases, operators will add the flocculant to an overflow solution which is to be blended with the corresponding underflow. While this is very effective for good flocculation, it can result in reflocculation of the solids before the entrained liquor has had a chance to blend completely with the overflow liquor. The preferable procedure is to recycle a portion of the overflow back to the feed line of the same thickener, adding the reagent to this liquor.

The usual method of interstage mixing consists of a relatively simple arrangement in which the flows from preceding and succeeding stages are added to a feed box at the thickener periphery. A nominal detention time in this mixing tank of 30 to 60 s and sufficient energy input to avoid solids settling will ensure interstage efficiencies greater than 95 percent.

The performance of a CCD circuit can be estimated through use of the following equations, which assume 100 percent stage efficiency:

$$R = \frac{O/U[(O/U)^N - 1]}{[(O/U)^{N+1} - 1]} \tag{18-49}$$

$$R = 1 - \left(\frac{U}{O'}\right)^N \tag{18-50}$$

for O/U and $U/O' \neq 1$. R is the fraction of dissolved value in the feed which is recovered in the overflow liquor from the first thickener, O and U are the overflow and underflow liquor volumes per unit weight of underflow solids, and N is the number of stages. Equation (18-49) applies to a system in which the circuit receives dry solids with which the second-stage thickener overflow is mixed to extract the soluble component. In this instance, O' refers to the overflow volume from the thickeners following the first stage.

For more precise values, computer programs can be used to calculate soluble recovery as well as solution compositions for conditions that are typical of a CCD circuit, with varying underflow concentrations, stage efficiencies, and solution densities in each of the stages. The calculation sequence is easily performed by utilizing material-balance equations around each thickener.

DESIGN OR STIPULATION OF A SEDIMENTATION UNIT

Selection of Type of Thickener or Clarifier Selection of the type of unit thickener or clarifier depends primarily on the optimization of performance requirements, installation cost and operating cost. For example, the inclined-plate type of clarifier provides for less solids-holding capacity than a circular or rectangular clarifier, but at a lower installation cost. The high-density thickener maximizes underflow solids concentration, requiring a higher torque rating than conventional thickeners.

Most manufacturers have overlapping sizes in the bridge-supported, center-column-supported, and traction types even though an optimum economical size range exists for each type. Bridge-supported thickeners are generally selected for diameters less than 30 m (100 ft) and center-column-supported thickeners are selected for greater diameters. Traction units often are least expensive in sizes over 75 m (250 ft) if ground conditions permit installing proper supporting walls to carry the loads.

Special conditions affect the choice of thickener or clarifier type. For example, if a unit must be covered to conserve heat, the bridge-supported type may be more economical up to about 45 m (150 ft) in diameter, although 30 m (100 ft) may be the economic limit for an uncovered unit.

Materials of Construction A wide variety of materials is available for tanks, as indicated earlier. Most mechanisms are made of steel; however, submerged parts may be made of wood, stainless steel, rubber-covered or coated steel, or special alloys.

Design Sizing Criteria Table 18-7, which lists typical design sizing criteria and operating conditions for a number of thickener and clarifier applications, is presented for purposes of illustration or preliminary estimate. Actual thickening and clarification performance is dependent on particle size distribution, specific gravity, sludge bed compaction characteristics, and other factors. Final designs should be based on bench-scale tests involving the methods previously discussed.

If a solids-contact clarifier is required, the surface-area requirement must exclude the area taken up by the reaction chamber. The reaction chamber itself is normally sized for a detention time of 15 to 45 min, depending on the type of treatment and the design of the unit.

Torque Rating The choice of torque rating has been discussed earlier. Torque is a function of such factors as quantity and quality of underflow (therefore, of such parameters as particle characteristics and flocculant dosage that affect underflow character), unit area, and rake speed; but, in the final analysis, torque must be specified on the basis of experience modified by these factors. Unless one is experienced in a given application, it is wise to consult a thickener or clarifier manufacturer.

THICKENER COSTS

Equipment Costs vary widely for a given diameter because of the many types of construction. As a general rule, the total installed cost will be about 3 to 4 times the cost of the raking mechanism (including drivehead and lift), plus walkways and bridge or centerpier cage, railings, and overflow launders. Figure 18-93 shows the approximate installed costs of thickeners up to 107 m (350 ft) in diameter. These costs are to be used only as a guide. They include the erection of mechanism and tank plus normal uncomplicated site preparation, excavation, reinforcing bar placement, backfill, and surveying. The price does not include any electrical work, pumps, piping, instrumentation, walkways, or lifting mechanisms. Special design modifications, which are not in the price, could include elevated tanks (for underflow handling); special feedwell designs to control dilution, entrance velocity, and turbulence; electrical and drive enclosures required because of climatic conditions; and mechanism designs required because of scale buildup tendencies.

Operating Costs Power cost for a continuous thickener is an almost insignificant item. For example, a unit thickener 60 m (200 ft) in diameter with a torque rating of 1.0 MN·m (8.8 Mlbf·in) will normally require 12 kW (16 hp). The low power consumption is due to the very slow rotative speeds. Normally, a mechanism will be designed for a peripheral speed of about 9 m/min (0.5 ft/s), which corresponds to only 3 r/h for a 60-m (200-ft) unit. This low speed also means very low maintenance costs. Operating labor is low because little attention is normally required after initial operation has balanced the feed and underflow. If chemicals are required for flocculation, the chemical cost frequently dwarfs all other operating costs.

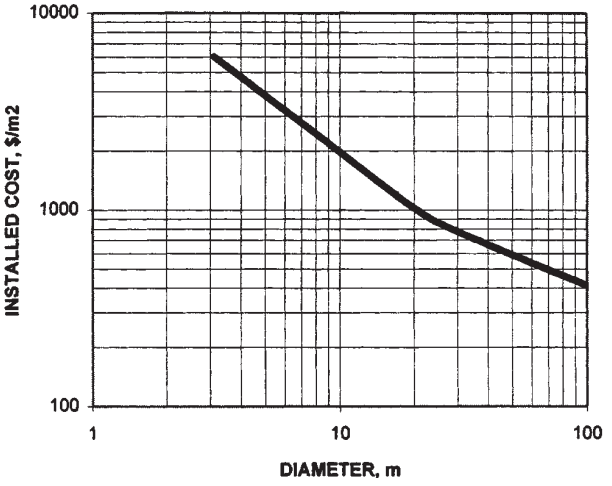


FIG. 18-93 Approximate installed cost of single-compartment thickeners (1995 dollars). To convert to ft and ft^2 units, multiply diameter in meters by 3.28 and divide cost by 10.76.

FILTRATION

General References: Moir, *Chem. Eng.*, **89**(15), 46 (1982). Brown, ibid., 58; also published as McGraw-Hill Repr. A078. Cheremisinoff and Azbel, *Liquid Filtration,* Ann Arbor Science, Woburn, Mass., 1983. Orr (ed.), *Filtration: Principles and Practice,* part I, Marcel Dekker, New York, 1977; part II, 1979. Purchas (ed.), *Solid/Liquid Separation Equipment Scale-Up,* Uplands Press, Croydon, England, 1977. Schweitzer (ed.), *Handbook of Separation Techniques for Chemical Engineers,* part 4, McGraw-Hill, New York, 1979. Shoemaker (ed.), "What the Filter Man Needs to Know about Filtration," *Am. Inst. Chem. Eng. Symp. Ser.,* **73**(171), (1977). Talcott et al., in *Kirk-Othmer Encyclopedia of Chemical Technology,* 3d ed., vol. 10, Wiley, New York, 1980, p. 284. Tiller et al., *Chem. Eng.,* **81**(9), 116–136 (1974); also published as McGraw-Hill Repr. R203.

DEFINITIONS AND CLASSIFICATION

Filtration is the separation of a fluid-solids mixture involving passage of most of the fluid through a porous barrier which retains most of the solid particulates contained in the mixture. This subsection deals only with the filtration of solids from liquids; gas filtration is treated in Sec. 17. **Filtration** is the term for the unit operation. A filter is a piece of unit-operations equipment by which filtration is performed. The **filter medium** or **septum** is the barrier that lets the liquid pass while retaining most of the solids; it may be a screen, cloth, paper, or bed of solids. The liquid that passes through the filter medium is called the **filtrate.**

Filtration and filters can be classified several ways:

1. *By driving force.* The filtrate is induced to flow through the filter medium by hydrostatic head (gravity), pressure applied upstream of the filter medium, vacuum or reduced pressure applied downstream of the filter medium, or centrifugal force across the medium. Centrifugal filtration is closely related to centrifugal sedimentation, and both are discussed later under "Centrifuges."
2. *By filtration mechanism.* Although the mechanism for separation and accumulation of solids is not clearly understood, two models are generally considered and are the basis for the application of theory to the filtration process. When solids are stopped at the surface of a filter medium and pile upon one another to form a cake of increasing thickness, the separation is called **cake filtration.** When solids are trapped within the pores or body of the medium, it is termed **depth, filter-medium,** or **clarifying filtration.**
3. *By objective.* The process goal of filtration may be dry solids (the cake is the product of value), clarified liquid (the filtrate is the product of value), or both. Good solids recovery is best obtained by cake filtration, while clarification of the liquid is accomplished by either depth or cake filtration.
4. *By operating cycle.* Filtration may be intermittent (batch) or continuous. Batch filters may be operated with constant-pressure driving force, at constant rate, or in cycles that are variable with respect to both pressure and rate. Batch cycle can vary greatly, depending on filter area and solids loading.
5. *By nature of the solids.* Cake filtration may involve an accumulation of solids that is compressible or substantially incompressible, corresponding roughly in filter-medium filtration to particles that are deformable and to those that are rigid. The particle or particle-aggregate size may be of the same order of magnitude as the minimum pore size of most filter media (1 to 10 μm and greater), or may be smaller (1 μm down to the dimension of bacteria and even large molecules). Most filtrations involve solids of the former size range; those of the latter range can be filtered, if at all, only by filter-medium-type filtration or by ultrafiltration unless they are converted to the former range by aggregation prior to filtration.

These methods of classification are not mutually exclusive. Thus filters usually are divided first into the two groups of cake and clarifying equipment, then into groups of machines using the same kind of driving force, then further into batch and continuous classes. This is the scheme of classification underlying the discussion of filters of this subsection. Within it, the other aspects of operating cycle, the nature of the solids, and additional factors (e.g., types and classification of filter media) will be treated explicitly or implicitly.

FILTRATION THEORY

While research has developed a significant and detailed filtration theory, it is still so difficult to define a given liquid-solid system that it is both faster and more accurate to determine filter requirements by performing small-scale tests. Filtration theory does, however, show how the test data can best be correlated, and extrapolated when necessary, for use in scale-up calculations.

In cake or surface filtration, there are two primary areas of consideration: continuous filtration, in which the resistance of the filter cake (deposited process solids) is very large with respect to that of the filter media and filtrate drainage, and batch pressure filtration, in which the resistance of the filter cake is not very large with respect to that of the filter media and filtrate drainage. Batch pressure filters are generally fitted with heavy, tight filter cloths plus a layer of precoat and these represent a significant resistance that must be taken into account. Continuous filters, except for precoats, use relatively open cloths that offer little resistance compared to that of the filter cake.

Simplified theory for both batch and continuous filtration is based on the time-honored Hagen-Poiseuille equation:

$$\frac{1}{A}\frac{dV}{d\Theta} = \frac{P}{\mu(\alpha w V/A + r)} \tag{18-51}$$

where V is the volume of filtrate collected, Θ is the filtration time, A is the filter area, P is the total pressure across the system, w is the weight of cake solids/unit volume of filtrate, μ is the filtrate viscosity, α is the cake-specific resistance, and r is the resistance of the filter cloth plus the drainage system.

CONTINUOUS FILTRATION

Since testing and scale-up are different for batch and continuous filtration, discussion in this section will be limited to continuous filtration.

It is both convenient and reasonable in continuous filtration, except for precoat filters, to assume that the resistance of the filter cloth plus filtrate drainage is negligible compared to the resistance of the filter cake and to assume that both pressure drop and specific cake resistance remain constant throughout the filter cycle. Equation (18-51), integrated under these conditions, may then be manipulated to give the following relationships:

$$W = \sqrt{\frac{2wP\Theta_f}{\mu(\alpha w V/A + r)}} \tag{18-52}$$

$$V_f = \sqrt{\frac{2P\Theta_f}{\mu\alpha w}} \tag{18-53}$$

$$\Theta_w = \frac{WV_W\mu\alpha}{P_w} \tag{18-54}$$

$$\Theta_W \propto NW^2 \tag{18-55}$$

$$\frac{\Theta_W}{\Theta_f} = 2\,\frac{V_W}{V_f} \tag{18-56}$$

where W is the weight of dry filter cake solids/unit area, V_f is the volume of cake formation filtrate/unit area, V_w is the volume of cake wash filtrate/unit area, Θ_f is the cake formation time, Θ_w is the cake wash time, and N is the wash ratio, the volume of cake wash/volume of liquid in the discharged cake.

As long as the suspended solids concentration in the feed remains constant, these equations lead to the following convenient correlations:

$$\log W \text{ vs. } \log \Theta_f \tag{18-57}$$

$$\log V_f \text{ vs. } \log \Theta_f \tag{18-58}$$

$$\Theta_w \text{ vs. } WV_w \tag{18-59}$$

$$\Theta_w \text{ vs. } NW^2 \tag{18-60}$$

$$\Theta_{w/f} \text{ vs. } V_w/V_f \tag{18-61}$$

There are two other useful empirical correlations as follows:

$$W \text{ vs. cake thickness} \tag{18-62}$$

$$\log R \text{ vs. } N \tag{18-63}$$

where R is percent remaining—the percent of solute in the unwashed cake that remains after washing.

FACTORS INFLUENCING SMALL-SCALE TESTING

[Purchas (ed.), *Solid/Liquid Separation Equipment Scale-Up*, Uplands Press, Croydon, England, 1977.]

Vacuum or Pressure The vast majority of all continuous filters use vacuum to provide the driving force for filtration. However, if the feed slurry contains a highly volatile liquid phase, or if it is hot, saturated, and/or near the atmospheric pressure boiling point, the use of pressure for the driving force may be required. Pressure filtration might also be used where the required cake moisture content is lower than that obtainable with vacuum.

The objective of most continuous filters is to produce a dry or handleable cake. Most vacuum filters easily discharge a "dry" consolidated cake as they are usually operated in an open or semiopen environment. However, whenever the filter must operate under pressure or within a vapor-tight enclosure, either because of the need for a greater driving force or because of the vapor pressure of the liquid phase, a dry cake discharge becomes difficult. The problem of removing a dry cake from a pressurized enclosure has precluded the use of continuous-pressure filters in many cases where this is a requirement. Applications which do discharge dry cake from a "sealed" enclosure are restricted to relatively dry, friable cakes that will "flow" through double valves which form a "vapor lock."

Cake Discharge For any filter application to be practical, it must be possible to produce a cake thick enough to discharge. Table 18-8 tabulates the minimum acceptable cake thickness required for discharge for various types of filters and discharge mechanisms. The experimenter, when running small-scale tests, should decide early in the test program which type of discharge is applicable and then tailor the data collected to fit the physical requirements of that type of unit. Note, however, that the data correlations recommended later are sufficiently general in nature to apply to most equipment types.

Feed Slurry Temperature Temperature can be both an aid and a limitation. As temperature of the feed slurry is increased, the viscosity of the liquid phase is decreased, causing an increase in filtration rate and a decrease in cake moisture content. The limit to the benefits of increased temperature occurs when the vapor pressure of the liquid phase starts to materially reduce the allowable vacuum. If the liquid phase is permitted to flash within the filter internals, various undesired results may ensue: disruption in cake formation adjacent to the medium, scale deposit on the filter internals, a sharp rise in pressure drop within the filter drainage passages due to increased vapor flow, or decreased vacuum pump capacity. In most cases, the vacuum system should be designed so that the liquid phase does not boil.

In some special cases, steam filtration can be used to gain the advantages of temperature without having to heat the feed slurry. Where applicable, dry steam is passed through the deliquored cake to raise the temperature of the residual moisture, reduce its viscosity, and lower its content. The final drying or cooling period which follows steam filtration uses the residual heat left in the cake to evaporate some additional moisture.

TABLE 18-8 Minimum Cake Thickness for Discharge

Filter type	Minimum design thickness	
	mm	in
Drum		
Belt	3–5	1/8–3/16
Roll discharge	1	1/32
Std. scraper	6	1/4
Coil	3–5	1/8–3/16
String discharge	6	1/4
Precoat	0–3 max.	0–1/8 max.
Horizontal belt	3–5	1/8–3/16
Horizontal table	20	3/4
Tilting pan	20–25	3/4–1
Disk	10–13	3/8–1/2

Cake Thickness Control Sometimes the rate of cake formation with bottom feed–type filters is rapid enough to create a cake too thick for subsequent operations. Cake thickness may be controlled by adjusting the bridge-blocks in the filter valve to decrease the effective submergence, by reducing the slurry level in the vat, and by reducing the vacuum level in the cake formation portion of the filter valve. If these measures are inadequate, it may be necessary to use a top-loading filter.

Cake thickness must frequently be restricted when cake washing is required or the final cake moisture content is critical. Where the time required for cake washing is the rate-controlling step in the filter cycle, maximum filtration rate will be obtained when using the minimum cake thickness that gives good cake discharge. Where minimum cake moisture content is the controlling factor, there is usually some leeway with respect to cake thickness, although the minimum required for cake discharge is controlling in some cases. Since a relatively constant quantity of moisture is transferred from the medium to the filter cake when the vacuum is released prior to cake discharge, very thin cakes will sometimes be wetter than thicker cakes.

The effect of an increase in cake thickness on the time required for washing is easy to see if one considers what happens when the cake thickness is doubled. Assume that two cakes have the same permeability and that the quantity of washing fluid to cake solids is to remain constant. Doubling of the cake thickness doubles the resistance to flow of the washing fluid through the cake. At the same time, the quantity of washing fluid per unit area is also doubled. Thus, the time required for the washing fluid to pass through the cake is increased by the square of the ratio of the cake thicknesses. In this particular example, the washing time would be increased by a factor of four, while cake production would only be doubled.

Filter Cycle Each filter cycle is composed of cake formation plus one more of the following operations: deliquoring (dewatering or drying), washing, thermal drying, steam drying, and cake discharge. The number of these operations required by a given filtration operation depends upon the process flowsheet. It is neither possible nor necessary to consider all of these operations at once. The basic testing program is designed to look at each operation individually. The requirements for each of the steps are then fit into a single filter cycle.

All filters utilizing a rotary filter valve have their areas divided into a number of sections, sectors, or segments (see Fig. 18-122). When a drainage port passes from one portion of the filter valve to another, the change at the filter medium does not occur instantaneously nor does it occur at some precise location on the filter surface. The change is relatively gradual and occurs over an area, as the drainage port at the filter valve first closes by passing onto a stationary bridge-block and then opens as it passes off that bridge-block on the other side.

On a horizontal belt filter, the equivalent sections extend across the filter in narrow strips. Therefore, changes in vacuum do occur rapidly and may be considered as happening at a particular point along the length of the filter.

Representative Samples The results which are obtained in any bench-scale testing program can be only as good as the sample which is tested. It is absolutely essential that the sample used be representative of the slurry in the full-scale plant and that it be tested under the conditions that prevail in the process. If there is to be some significant time between taking or producing the sample and commencing the test program, due consideration must be given to what effect this time lapse may have on the characteristics of the slurry. If the slurry is at a temperature different from ambient, the subsequent heating and/or cooling could change the particle size distribution. Even sample age itself may exert a significant influence on particle size. If there is likely to be an effect, the bench-scale testing program should be carried out at the plant or laboratory site on fresh material.

Whenever a sample is to be held for some time or shipped to a distant laboratory for testing, some type of characterizing filtration test should

be run on the fresh sample and then duplicated at the time of the test program. A comparison of the results of the two tests will indicate how much of a change there has been in the sample. If the change is too great, there would be no point in proceeding with the tests, and it would be necessary to make arrangements to work on a fresh sample. Any shipped sample, especially during the winter months, must be protected from freezing, as freezing can substantially change the filtration characteristics of a slurry, *particularly hydrated* materials.

The slurry should always be defined as completely as possible by noting suspended solids concentration, particle size distribution, viscosity, density of solids and liquid, temperature, chemical composition, and so on.

Feed Solids Concentration Feed slurries that are so dilute that they settle rapidly usually yield reduced solids filtration rates and produce stratified cakes with higher moisture contents than would normally be obtained with a homogeneous cake. It is well known that an increase in feed solids concentration is generally an effective means of increasing solids filtration rate, assisting in forming a homogeneous suspension and thereby minimizing cake moisture content, and so on. Equipment required to concentrate a slurry sample and the tests needed to predict how far a slurry will thicken are discussed elsewhere in this section.

Pretreatment Chemicals Even though the suspended solids concentration of the slurry to be tested may be correct, it is frequently necessary to modify the slurry in order to provide an acceptable filtration rate, washing rate, or final cake moisture content. The most common treatment, and one which may provide improvement in all three of these categories, is the addition of flocculating agents, either inorganic chemicals or natural or synthetic polymers. The main task at this point is to determine which is the most effective chemical and the quantity of chemical which should be used.

It is usually difficult to observe visually a change in floc structure in a concentrated slurry. The two best indications that an effective quantity of chemical has been added is a sudden thickening or increase in viscosity of the slurry and the formation of *riverlets* on the surface of a spatula when treated slurry is shaken from it. It is generally necessary to exceed a threshold quantity of chemical before there is a measurable improvement. The proper dosage becomes an economic balance between the cost of additional chemicals and the savings resulting from a reduction in filter area.

Screening tests are used to determine the best chemical and its approximate dosage. It is usually convenient to use small, graduated beakers and sample quantities in the range of 50 to 150 mL. The chemical may be added with a syringe or medicine dropper and a note made of the quantity used, together with the results. The experimenter should filter and wash the flocculated sample on any convenient, small, top-loading filter with good filtrate drainage. The cake formation and wash times obtained from these micro tests are not intended to provide sizing data, but they do provide an excellent indication of the relative effectiveness of various chemicals and treatment levels.

With any chemical treatment system, the main task is one of getting the chemical thoroughly mixed with the solids without degrading the flocs which are formed. For those slurries that are relatively fluid, the chemical can frequently be added and mixed satisfactorily using a relatively wide spatula. However, for those thick, relatively viscous slurries, a power mixer will be required. In this case, the mixer should be stopped about one second after the last of the flocculant is added. Should this approach be required, it means that a suitably designed addition system must be supplied with the full-scale installation in order to do an effective job of flocculation.

While the volume of chemical used should be minimized, the experimenter must use good judgment based on the viscosities of both the slurry to be treated and the chemical used. If both are relatively viscous, use of a power mixer is indicated.

There are a number of commercially available surfactants that can be employed as an aid in filter cake moisture reduction. These reagents can be added to the filter feed slurry or to the filter cake wash water, if washing is used. Since these reagents have a dispersing effect, flocculation may be required subsequently. Typical moisture reductions of 2 to 4 percentage points are obtained at reagent dosages of 200 to 500 g/mt of solids.

Cloth Blinding Continuous filters, except for precoats, generally use some type of medium to effect the separation of the solid and filtrate phases. Since the medium is in contact with the process solids, there is always the danger, and almost invariably the actual occurrence, of medium blinding. The term **blinding** refers to blockage of the fabric itself, either by the wedging of process solids or by solids precipitated in and around the yarn.

The filter medium chosen should be as open as possible yet still able to maintain the required filtrate clarity. Those fabrics which will produce a clear filtrate and yet do not have rapid blinding tendencies are frequently light in weight (woven from thin filaments or yarn) and will not wear as long as some of the heavier, more open fabrics (woven from heavy filaments or yarn). Whenever the filter follows a gravity thickening or clarification step, it is advisable to return the filtrate to the thickener or clarifier so that the filtrate clarity requirements may be relaxed in favor of using a heavier, more open cloth with reduced blinding tendencies. Excessively dirty filtrates should be avoided as the solids may be abrasive and detrimental to the internals of the filter or perhaps may cut the fabric yarn.

It should be noted at this point that an **absolutely** clear filtrate can rarely be obtained on a cloth-covered continuous filter. The passages through the medium are invariably larger than some of the solids in the slurry, and there will be some amount of solids passing through the medium. Once the pores of the fabric have been bridged, the solids themselves form the septum for the remaining particles, and the filtrate becomes clear. It is this bridging action of the solids that permits the use of a relatively open filter medium, while at the same time maintaining a reasonably clear filtrate.

Filters with media in the form of an endless belt have greatly reduced the concern about blinding. Most synthetic fabrics can be successfully cleaned of process solids by washing the medium after cake discharge, and the rate of blinding due to chemical precipitation also can be drastically reduced. Current practice suggests that the belt-type filter with continuous-medium washing be the first choice unless experience has shown that medium blinding is not a factor or if the belt-type system cannot be successfully applied.

Sealing of the belt along the edges of the filter drum is never perfect, and some leakage should be expected. If good clarity is essential, it may be preferable to use a drum filter with the cloth caulked in place and design the system to contend with the effects of blinding.

The one exception to the points noted above is the continuous precoat filter. Here the purpose of the filter medium is to act as a support for the sacrificial bed of precoat material. Thus, the medium should be tight enough to retain the precoat solids and prevent bleeding of the precoat solids through the filter medium during operation, yet open enough to permit easy cleaning at the end of each cycle. Lightweight felt media work well in these respects.

Homogeneous Cake Accurate test results and optimum filter performance require the formation of a homogeneous cake and thus the maintenance of a similarly homogeneous suspension. Settling in the sample container during a bottom-feed test program can usually be detected by comparing the back-calculated feed solids concentration (based on filtrate, wet cake, and dry cake weights) with the slurry solids concentration as prepared. It is normal to find that the back-calculated concentration is slightly lower than the prepared concentration. This difference is normally within 2 percentage points and should never be greater than 5 percentage points. Since this difference does exist, it means that the slurry sample will concentrate to some extent as the tests continue. Adding fresh slurry to the sample container after each test can counteract this condition, as the system will reach an equilibrium similar to that found in a full-scale machine.

If a more positive check is required on the quality of the filter cake, particle size analyses may be run and compared with the sample as prepared.

In a top-feed filter test, the filter cake will contain all of the solids, provided they are all emptied from the sample container. The danger in this type of test is that the solids will stratify, particularly if the cake formation time is prolonged. Close examination of the filter cake will

indicate whether or not this has happened. If there has been significant stratification, the feed slurry should be modified by thickening and/or flocculation in order to increase the dry solids filtration rate and permit formation of a homogeneous cake. Another possibility, but not necessarily the best, is to use a thinner, but still dischargeable, cake to avoid stratification.

Agitation of Sample All slurries used in bottom-feed tests must be agitated by hand (if slurry characteristics permit) to check whether or not the solids are settling out around the edges of the container and to determine the degree of agitation required to maintain the solids in suspension. Generally speaking, if the solids can be maintained in suspension by hand agitation, the slurry can be processed by a bottom-feed-type filter.

Agitation by a wide spatula may be substituted for hand agitation, but only after it has been determined by feel that the spatula will provide the needed agitation. If this cannot be done, then confirmation of proper agitation must be based on back-calculated feed solids concentrations and/or particle size analyses of the filter cakes.

If it is not possible to maintain a uniform suspension, the sample should be thickened and the flowsheet modified to provide the required thickening.

Mechanical agitation of a sample is very difficult to use effectively. Generally speaking, if enough room is left in the sample container for the leaf and the agitator, the agitation is not sufficient to prevent settling out in the corners of the container. If sufficient agitation is used to maintain suspension in all parts of the container, then it is highly probable that the velocity of the slurry across the face of the test leaf will wash the solids from the leaf and give very erroneous results. Furthermore, the tendency is to leave the agitator running continuously, or at least for so long a period of time that there is attrition of the solids and, therefore, inaccurate results. Mechanical agitation during testing can generally be justified only in a most unusual and exceptional circumstance.

Use of Steam or Hot Air It was indicated earlier that the cycle might include steam filtration or thermal drying using hot air. While effective use is made of both steam and hot air, the applications are rather limited, and testing procedures are difficult and specialized. As a general rule, steam application will reduce cake moisture 2 to 4 percentage points. Hot-air drying can produce a bone-dry cake, but generally it is practical only if the air rate is high, greater than about 1800 $m^3/m^2 \cdot h$ (98 cfm/ft^2). Both systems require a suitable hood which must contact the dam on the leaf during the drying cycle, allowing the steam or hot air to pass through the cake without dilution by cold air. The end of the operation can be determined by a noticeable increase in the temperature of the gas leaving the leaf.

SMALL-SCALE TEST PROCEDURES

[Purchas (ed.), *Solid/Liquid Separation Equipment Scale-Up*, Uplands Press, Croydon, England, 1977.]

Apparatus There are several variations of the bench-scale test leaf that may be used, but they all have features similar to the one discussed below.

One typical test leaf is a circular disk with a plane area of 92.9 cm^2 (0.1 ft^2). One face of the leaf is grooved to provide large filtrate drainage passages and a support for the filter medium. A threaded drainage connection is provided on the center of the other face of the leaf. The test leaf is fitted with a filter medium and a dam, and the assembly clamped together as shown in Fig. 18-94. The depth of the dam for bottom-feed tests should be no greater than the depth of the maximum cake thickness, except where cake washing tests are to be performed. In this case, the dam depth should be about 3 mm (⅛ in) greater than the maximum expected cake thickness. Excessive dam depth will interfere with slurry agitation and can result in the formation of a nonhomogeneous cake.

It is absolutely necessary that a dam be used in all cases, except for roll discharge applications which do not involve cake washing or where the maximum cake thickness is on the order of 2 mm or less. If a dam is not used, filter cake will form past the edge of the leaf in the general shape of a mushroom. When this happens, the total filter area is some unknown value, greater than the area of the leaf, that constantly increases with time during cake formation.

The back of the leaf assembly and the joint where the dam overlaps must be sealed with some suitable material so that the filtrate volume collected accurately represents the liquid associated with the deposited cake solids.

Figure 18-95 also contains a schematic layout of the equipment which is required for all bottom-feed leaf tests. Note that there are no valves in the drainage line between the test leaf and the filtrate receiver, nor between the filtrate receiver and the vacuum pump.

At the start of the leaf test run, the hose between the test leaf and filtrate receiver should be crimped by hand to bring the filtrate receiver to the operating vacuum level. The use of a valve at this point is not only less convenient but very frequently results in a hydraulic

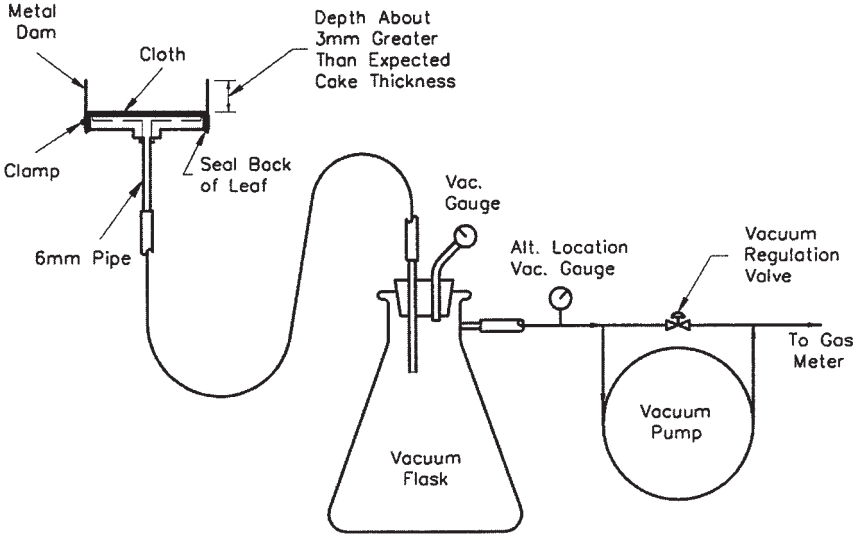


FIG. 18-94 Typical bottom-feed leaf test setup.

restriction. The net result, then, is a measurement of flow through the valve rather than the rate at which the filter cake is capable of forming. Hydraulic restriction is something which should always be kept in mind. If the filtrate runs at a high and full pipe flow rate into the filtrate receiver, it is quite likely that there is some degree of hydraulic restriction, and larger tubing and piping should be considered. When very high air flow rates are obtained, the experimenter must be satisfied that the rates being measured are limited by cake resistance and not by pressure drop through the equipment.

There will be many times when the quantity of sample is limited. While it is best to use the 92.9 cm^2 (0.1 ft^2) area leaf in order to minimize edge effects and improve accuracy, when the sample volume is limited it is much better to have several data points with a smaller leaf than only one or two using the larger leaf. Data from leaves as small as 23.2 cm^2 (0.025 ft^2) are reasonably accurate and can be used to scale up to commercially sized units. However, it is usually prudent to employ a more conservative scale-up factor.

For top-feed applications, the most convenient assembly is that shown in Fig. 18-95. The depth of the dam must, of course, be sufficient to contain the total quantity of feed slurry required for the test. Since the test leaf is mounted on top of the vacuum receiver, it is necessary to provide a valve between the test leaf and the receiver so that the desired operating vacuum may be obtained in the receiver before the start of a test run. It is imperative, however, that there be no restriction in this valve. The preferred choice is a ball valve with the full bore of the drainage piping.

Test Program Figure 18-96 is a suggested data sheet which contains spaces for most of the information which should be taken during a leaf test program, together with space for certain calculated values. Additional data which may be required include variations in air flow rate through the cake during each dewatering period and chemical and physical data for those tests involving cake washing.

It is difficult to plan a filtration leaf test program until one test has been run. In the case of a bottom-feed test, the first run is normally started with the intention of using a 30-s cake formation time. However, if the filtrate rate is very high, it is usually wise to terminate the run at the end of 15 s. Should the filtrate rate be very low, the initial form period should be extended to at least 1 min. If cake washing is to be employed, it is useful to apply a quantity of wash water to measure its rate of passage through the cake. The results of this first run will give the experimenter an approximation of cake formation rate, cake washing rate, and the type of cake discharge that must be used. The rest of the leaf test program can then be planned accordingly.

In any leaf test program there is always a question as to what vacuum level should be used. With very porous materials, a vacuum in the range of 0.1 to 0.3 bar (3 to 9 in Hg) should be used, and, except for thermal-drying applications using hot air, the vacuum level should be adjusted to give an air rate in the range of 450 to 900 $m^3/m^2 \cdot h$ (30 to 40 cfm/ft^2) measured at the vacuum.

For materials of moderate to low porosity, a good starting vacuum level is 0.6 to 0.7 bar (18 to 21 in Hg), as the capacity of most vacuum pumps starts to fall off rapidly at vacuum levels higher than 0.67 bar (20 in Hg). Unless there is a critical moisture content which requires the use of higher vacuums, or unless the deposited cake is so impervious that the air rate is extremely low, process economics will favor operation at vacuums below this level. When test work is carried out at an elevation above sea level different than that of the plant, the elevation at the plant should be taken into account when determining the vacuum system capacity for high vacuum levels (>0.5 bar).

Generalized correlations are available for each of the operations which make up the full filter cycle. This means that simulated operating conditions can be varied to obtain a maximum of information without requiring an excessive number of test runs. The minimum number of test runs required for a given feed will, of course, vary with the expertise of the experimenter and the number of operations performed during the filter cycle. If, for example, the operation involves only the dewatering of a slurry which forms a cake of relatively low to moderate porosity, frequently sufficient data can be obtained in as little as six runs. For more difficult tests, more runs are usually advisable, and the novice certainly should make a larger number of runs as there is likely to be more data scatter.

Bottom-Feed Procedure The procedure for collecting data using bottom-feed leaf test techniques is as follows:

1. Fit the test leaf with a filter cloth expected to give reasonable results and seal the back of the leaf and side of the dam with silicone or other suitable material.

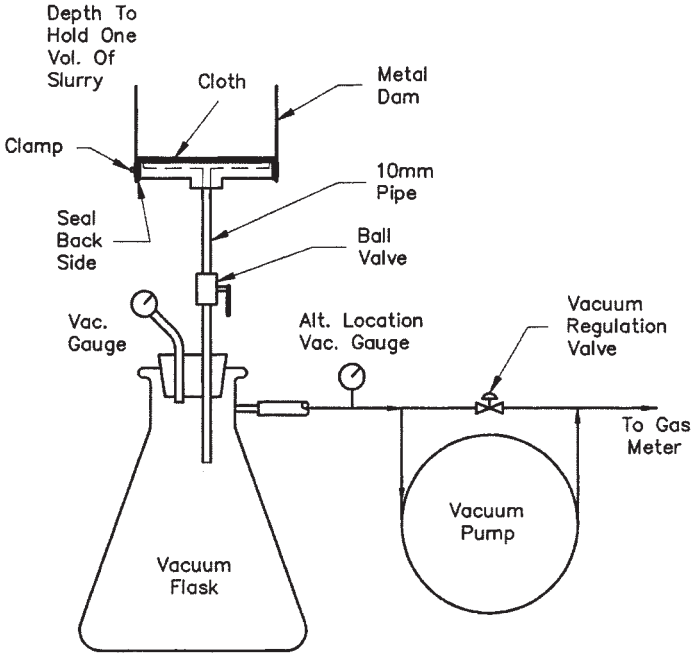


FIG. 18-95 Typical top-feed leaf test setup.

FILTRATION LEAF TEST DATA SHEET – VACUUM AND PRESSURE

Company _____ Mat'l as Received: Date _____ Test No. _____
Address _____ Solids: _____ % Date Tested _____
_____ Analysis _____ By _____
_____ Liquid: _____ % Location _____
Filter Type _____ Leaf Size _____ Ft.^{2} Analysis _____
Used Shim: No _____ Yes _____ Precoat Forming Liquid _____ Temp. _____ °F/°C

Run No.	Filter Module and/or Precoat Type	Feed Temp., °F/°C	% Solids in Food		Vacuum = in. Hg. Pressure = PSI.				TIME, MIN.					Air Flow		Filtrate		Precoat Penetration	Wash		Cake/Precoat Thickness, In.	Dia. of Shared Area, In.	Cake Weights			
			As Prepared	Back Calculated	Form	Wash	Dry	After Cake Cracks	Form	Dewater	Wash	Dry	To Crack or Gas Breakthrough After Form/Wash	(1)	Temp., °F/°C	ML.	Clarity		ML.	Temp., °F/°C			Tare GMS.	Wet & Tare GMS.	Dry & Tare GMS.	Dish No.

CAKE DISCHARGE		REAGENT TREATMENT	
RUNS	COMMENT	RUNS	COMMENT

REMARKS: (1) Record Basis of Observation in Space Provided.

FIG. 18-96 Sample data sheet.

2. Hand-crimp the hose in back of the test leaf, and then turn on the vacuum pump and regulate the bypass valve on the pump to give the desired vacuum level in the receiver.
3. Agitate the slurry by hand or with a wide spatula to maintain a homogeneous suspension. Immerse the test leaf face downward to approximately one-half the depth of the slurry.
4. Simultaneously start the timer and release the crimped hose to begin cake formation. Maintain agitation during cake formation and move the leaf as may be required to ensure that solids do not settle out in any part of the container. It is not necessary to try to simulate the velocity with which the full-scale unit's filtration surface passes through the slurry in the filter tank.
5. Remove the leaf from the slurry at the end of the cake-formation period and note the time. If the slurry is particularly thick and viscous, the leaf may be gently shaken to remove excess slurry and prevent the dam from scooping up extra material. Maintain the leaf in an upright position (cake surface on top) and elevated so that liquid within the drainage passages may pass to the receiver. Tilt and rotate the leaf to help the filtrate reach the drain outlet. Continue this dewatering period until:
   a. the preselected time has elapsed, or
   b. the cake cracks.
6. If the cake is to be washed, apply a measured quantity of wash fluid and note the time required for free fluid to disappear from the surface of the cake. Pour the wash fluid onto a deflecting baffle, such as a bent spatula, to prevent the cake from being gouged. Washing must begin before cake cracking occurs. In particular, observe that there is no crack along the edge between the cake and the dam.
7. Continue with the various operations in the predetermined sequence.
8. During each of the operations record all pertinent information such as vacuum level, temperature, time required for the cake to crack, filtrate foaming characteristics, air flow rate during the drying periods, etc.
9. At the end of the run, measure and record the filtrate volume (and weight, if appropriate), cake thickness, final cake temperature (if appropriate), wet cake weight, and note the cake discharge characteristics (roll, sticks to media, etc.).
10. For runs involving cake dewatering only, it is usually convenient to dry the total cake sample, if the associated solution contains little or no dissolved solids.
11. When cake washing is involved, it is usually convenient to weigh the wet cake and then repulp it in a known quantity of distilled water or in water at the same pH as the filtrate, if precipitation of

solute could occur in distilled water. The resultant slurry is then filtered using a clean dry filter and flask and a sample of the clear liquid analyzed for the reference constituent.

Should the mother liquor contain a significant quantity of dissolved solids, the filter cake should be thoroughly washed (after the sample for analysis has been taken) so that the final dry weight of the cake will represent suspended solids only. The quantity of reference constituent in the final washed cake can be readily calculated from the wet and dry cake weights and the known amount of distilled water used for repulping.

In cake-washing tests, it is important that the feed slurry liquid be analyzed for total dissolved solids and density as well as the reference constituent.

Top-Feed Procedure The sequence of operations with a top-feed leaf test is the same as in a bottom-feed test, except that the leaf is not immersed in the slurry. The best method for transferring the slurry to the top-feed leaf is, of course, a function of the characteristics of the slurry. If the particles in the slurry do not settle rapidly, the feed can usually be transferred to the leaf from a beaker. If, however, the particles settle very rapidly, it is virtually impossible to pour the slurry out of a beaker satisfactorily. In this case, the best method is to make use of an Erlenmeyer flask, preferably one made of plastic. The slurry is swirled in the flask until it is completely suspended and then abruptly inverted over the leaf. This technique will ensure that all of the solids are transferred to the leaf.

When the solids involved are coarse and fast settling, the vacuum should be applied an instant after the slurry reaches the surface of the filter medium.

Precoat Procedure Precoat filtration tests are run in exactly the same manner as bottom-feed tests except that the leaf must first be precoated with a bed of diatomaceous earth, perlite, or other shaveable inert solids. Some trial and error is involved in selecting a grade of precoat material which will retain the filtered solids to be removed on the surface of the bed without any significant penetration. During this selection process, relatively thin precoat beds of 1 to 2 cm are satisfactory. After a grade has been selected, bench-scale tests should be run using precoat beds of the same thickness as expected on the full-scale unit.

Where the resistance of the precoat bed is significant in comparison to the resistance of the deposited solids, the thickness of the precoat bed effectively controls the filtration rate. In some instances, the resistance of the deposited solids is very large with respect to even a thick precoat bed. In this case, variations in thickness through the life of the precoat bed have relatively little effect on filtration rate. This type of information readily becomes apparent when the filtration rate data are correlated.

The depth of cut involved in precoat filtration is a very important economic factor. There is some disagreement as to the method required to accurately predict the minimum permissible depth of cut. Some investigators maintain that the depth of cut can be evaluated only in a qualitative manner during bench-scale tests by judging whether the process solids remain on the surface of the precoat bed. This being so, they indicate that it is necessary to run a continuous pilot-plant test to determine the minimum permissible depth of cut. The use of a continuous pilot-plant filter is a very desirable approach and will provide accurate information under a variety of operating conditions.

However, it is not always possible to run a pilot-plant test in order to determine the depth of cut. A well-accepted alternative approach makes use of the more sophisticated test leaf illustrated in Fig. 18-97. This test leaf is designed so that the cake and precoat are extruded axially out the open end of the leaf. The top of the retaining wall on this end of the leaf is a machined surface which serves as a support for a sharp discharge knife. This approach permits variable and known depths of cut to be made so that the minimum depth of cut may be determined. Test units are available from Rutland Tool and Supply Company, City Of Industry, California, (800) 289-4787.

Lacking the above-described actual data, it is possible to estimate precoat consumption by using these values: nonpenetrating solids, 0.06-mm cut/drum revolution (0.0024 in); visible penetration, 0.15- to 0.20-mm cut/drum revolution (0.006 to 0.008 in); precoat bed density, 4.2 kg/m^2·cm of bed depth (2.2 lb/ft^2·in) for diatomaceous earth or 2.1 to 3.0 kg/m^2·cm (1.1 to 1.6 lb/ft^2·in) for perlite.

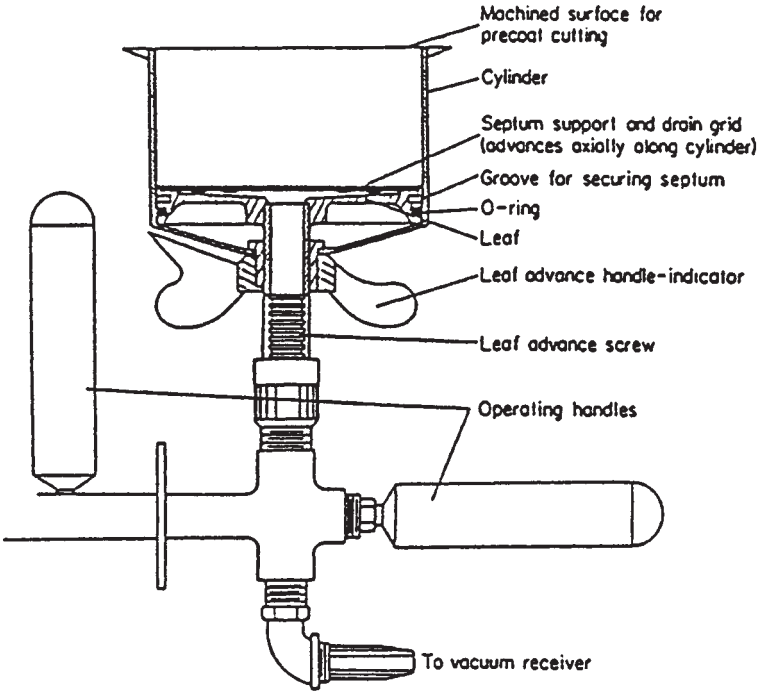


FIG. 18-97 Special test leaf for precoat filtration. (*Rutland Tool and Supply Company.*)

DATA CORRELATION

[Purchas (ed.), *Solid/Liquid Separation Equipment Scale-Up*, Uplands Press, Croydon, England, 1977.]

The correlations used are based partly on theoretical consideration and partly on empirical observations. The basic filtration data are correlated by application of the classic cake-filtration equation, aided by various simplifying assumptions which are sufficiently valid for many (but not all) situations. Washing and drying correlations are of a more empirical nature but with strong experimental justification. If steam or thermal drying is being examined, additional correlations are required beyond those summarized below; for such applications, it is advisable to consult an equipment manufacturer or refer to published technical papers for guidance.

Dry Cake Weight vs. Thickness It is convenient to convert the test dry cake weight to the weight of dry cake per unit area per cycle (*W*), and plot these values as a function of cake thickness (Fig. 18-98). Cake weight is measured quite accurately, while cake thickness measurements are subject to some variation. By plotting the data, variations in thickness measurements are averaged. The data usually give a straight line passing through the origin. However, with compressible material, sometimes a slightly curved line best represents the data, since thinner cakes are usually compressed more than thicker cakes.

Dry Solids or Filtrate Rate Filtration rate, expressed either in terms of dry solids or filtrate volume, may be plotted as a function of time on log-log paper. However, it is more convenient to delay the rate calculation until the complete cycle of operations has been defined.

It is most useful to plot either dry cake weight (weight of dry solids/unit area/cycle) or filtrate volume (volume/unit area/cycle) as a function of time on log-log paper. These data should give straight-line plots for constant operating conditions in accordance with Eqs. (18-52) and (18-53). The expected slope of the resultant rate/time plots is +0.50, as in Fig. 18-99. In practice, the vast majority of slopes range from +0.50 to +0.35. Slopes steeper than +0.5 indicate that there is some significant resistance other than that of the cake solids, such as a hydraulic restriction in the equipment or an exceptionally tight filter cloth.

Data from precoat tests, however, generally produce filtrate curves with much steeper slopes. The precoat bed has a greater resistance than most filter fabrics, and the particles which are separated on a continuous precoat usually form a cake which has a relatively low resistance when compared to that of the precoat bed. Once the thickness of the deposited solids becomes significant, their resistance increases. Thus, at very short form times, the slope of the filtrate curve

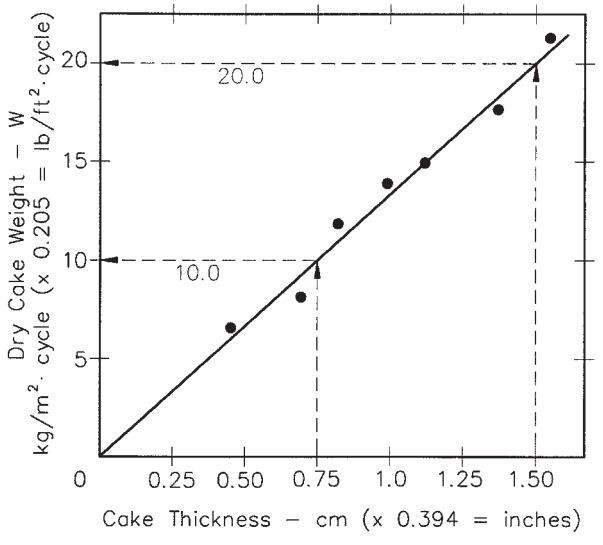


FIG. 18-98 Dry cake weight vs. cake thickness.

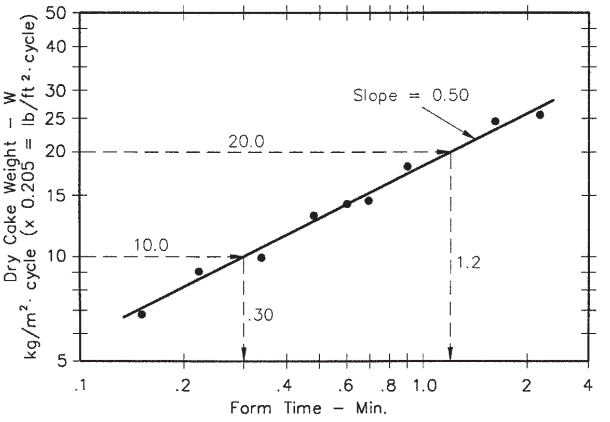


FIG. 18-99 Dry cake weight vs. form time.

may be close to 1.0, but as form time increases, the slope of the curve will decrease and will approach +0.5 (Fig. 18-100).

There are some solids, however, which form a less permeable cake, even in very thin layers. With these solids, the resistance of the deposited cake will be very high when compared to that of the precoat bed, and the slope of the filtrate curve will be +0.5 for all values of form time.

Effect of Time on Flocculated Slurries Flocculated slurries usually show significant decreases in filterability with time (Fig. 18-101). The rate of degradation may be established by running a series of repetitive leaf tests at frequent intervals on a flocculated slurry, starting as soon as practical after the addition of the flocculant. If there is little change in the filtration rate, this factor need be given no more consideration. However, it is usually found that there is significant degradation.

When a flocculated feed is added to a filter tank, there is a definite time lag before this material reaches the surface of the filter medium. Since this lag time is not known at the time of testing, a lag time of 8 to 10 minutes should be allowed before starting the first leaf test on a flocculated slurry. Two, or perhaps three, tests can be run before the elapsed time exceeds the probable retention time in the full-scale filter tank. With knowledge of the elapsed time after flocculation and data relating to the rate of degradation, the rates obtained on the leaf test runs can be adjusted to some constant lag time consistent with the anticipated full-scale design.

Cake Moisture Results on a wide variety of materials have shown that the following factor is very useful for correlating cake moisture content data:

$$\text{Correlating factor} = (m^3/m^2 \cdot h)(P_c/W)(\Theta_D/\mu), \qquad (18\text{-}64)$$

where $m^3/m^2 \cdot h$ = air rate through filter cake measured at downstream pressure or vacuum
P_c = pressure drop across cake
W = dry cake weight/unit area/cycle
Θ_D = dry time per cycle
μ = viscosity of liquid phase

For a more rigorous discussion of cake moisture correlation, the reader is referred to an earlier article by Nelson and Dahlstrom [*Chem. Eng. Progress*, **53,** 7, 1957]. Fig. 18-102 shows the general shape of the curve obtained when using the cake moisture correlating factor. The value of the correlating factor chosen for design should be somewhere past the knee of the curve. Values at and to the left of the knee are in an unstable range where a small change in operating conditions can result in a relatively large change in cake moisture content.

It is not always necessary to use all of the terms in the correlating factor, and those conditions which are held constant throughout the testing may be dropped from the correlating factor. Many times, air rate data are not available and reasonable correlations can be obtained

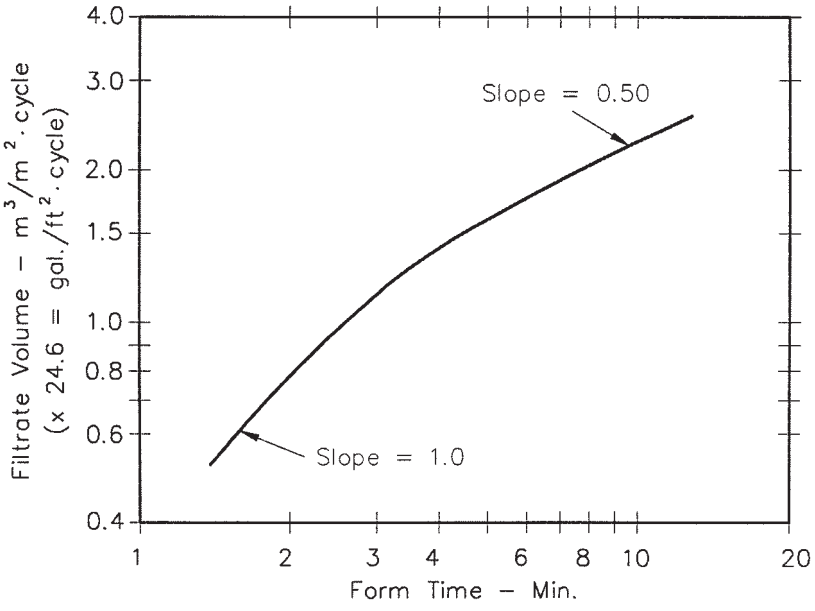


FIG. 18-100 Filtrate volume per cycle vs. form time.

without this information, particularly if the cakes are relatively low in permeability. By dropping these terms, the correlating factor is reduced to the simplified version, Θ_D/W, involving only drying time and cake weight per unit area per revolution. While this is a very convenient factor to use, care must be taken in its application, as it is no longer a generalized factor, and there will be a tendency for the data to produce different curves for changes in operating conditions such as vacuum level and cake thickness.

Cake Washing Wash efficiency data are most conveniently represented by a semilog plot of percent remaining R as a function of wash ratio N as shown in Fig. 18-103. Percent remaining refers to that portion of the solute in the dewatered but unwashed cake which is left in the washed and dewatered cake. Since a cake-washing operation involves the displacement of one volume of liquid by another volume, the removal of solute is related to the ratio of the volume of washing fluid divided by the volume of liquid in the cake. This ratio is defined as wash ratio N.

Practical experience has shown that the most convenient and best means of expressing R is in terms of the solute concentrations in the washed cake liquid, the feed liquid (or unwashed cake liquid), and the cake wash liquid. Furthermore, the wash ratio N may also be expressed either as a volume or weight ratio.

Percent remaining is defined as follows:

$$\frac{R}{100} = \frac{C_2 - C_w}{C_1 - C_w} \tag{18-65}$$

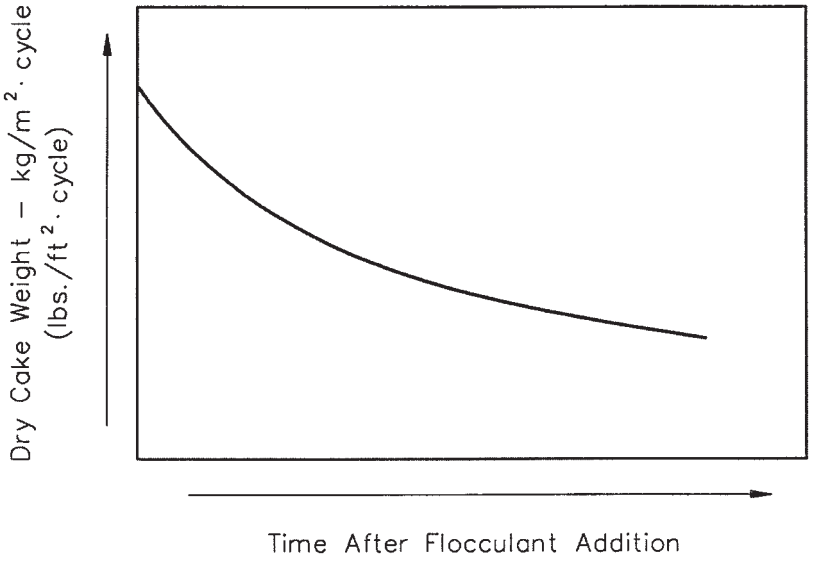


FIG. 18-101 Degradation of flocculation with time.

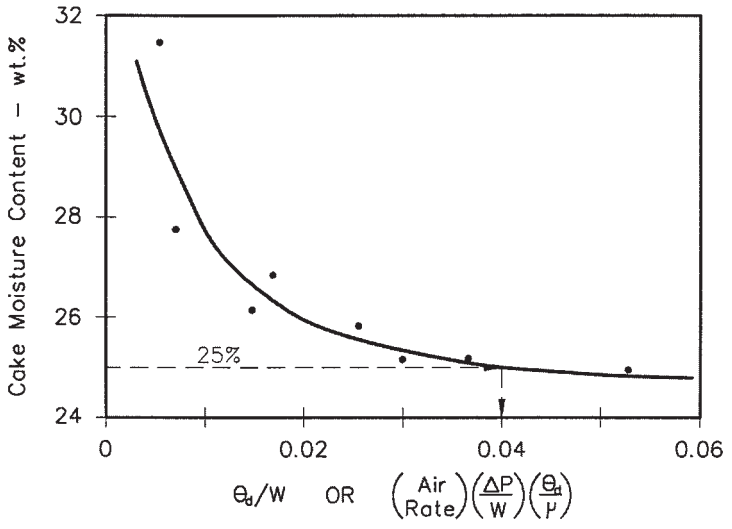


FIG. 18-102 Cake moisture correlation.

where R = % solute remaining after washing
C_2 = solute concentration in washed cake liquid
C_1 = solute concentration in unwashed cake liquid
C_w = solute concentration in wash liquid

If the cake is washed with solute-free liquid, percent remaining is readily calculated by dividing the solute concentration in the liquid remaining in the washed cake by the solute concentration in the liquid in the original feed.

The residence time of the cake-washing fluid within the cake is relatively short and is not normally considered useful for any kind of leaching operation. Therefore, it is assumed that all of the solute is in solution.

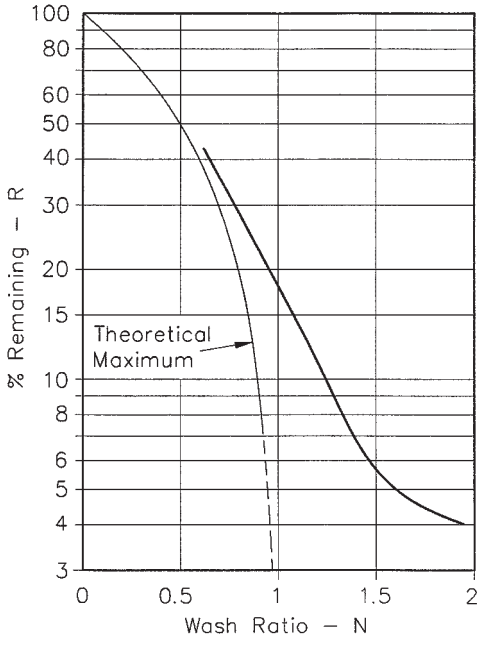


FIG. 18-103 Wash effectiveness.

If it were possible to obtain a perfect slug displacement wash, the fraction remaining would be numerically equal to 1 minus the wash ratio. This ideal condition is represented by the maximum theoretical line as shown in Fig. 18-103. Since it represents the best that can be done, no data point should fall to the left of this curve. Most, but not all, cake-washing curves tend to fall along the heavy solid line shown. In the absence of actual data, one may estimate washing results by using this curve.

The quantity of wash water to be used in a given operation is dictated by flowsheet considerations and the required solute content of the washed cake. Generally speaking, the maximum wash water quantity should be equivalent to a wash ratio of 1.5 to 2.5. Where high solute removals are required, it is frequently necessary to use a two-stage filtration system with intermediate repulping. These two stages may involve countercurrent flow of wash water, or fresh wash water may be used on both filters and for the intermediate repulping step.

Wash Time Cake-washing time is the most difficult of the filtration variables to correlate. It is obviously desirable to use one which provides a single curve for all of the data. Filtration theory suggests three possible correlations [Eqs. (18-59) to (18-61)]. These are listed below, beginning with the easiest to use:

1. Wash time vs. WV_w
2. Wash time vs. NW^2
3. Wash time/form time vs. wash volume/form volume

where W = weight dry cake/unit area/cycle
V_w = volume of cake wash/unit area/cycle
N = wash ratio
= volume of wash/volume of liquid in discharged cake

Fortunately, the easiest correlation to use usually gives satisfactory results. This curve is usually a straight line passing through the origin, but frequently falls off as the volume of wash water increases (Fig. 18-104). If for some reason this correlation is not satisfactory, one of the other two should be tried.

Air Rate Air rate through the cake, and thus vacuum pump capacity, can be determined from measurements of the air flow for various lengths of dry time. Figure 18-105 represents instantaneous air rate data. The total volume of gas passing through the cake during a dry period is determined by integrating under the curve.

Note that the air rate at the beginning of each drying or dewatering period within a given cycle starts at zero and then increases with time. The shape of this curve will be a function of the permeability of the deposited cake.

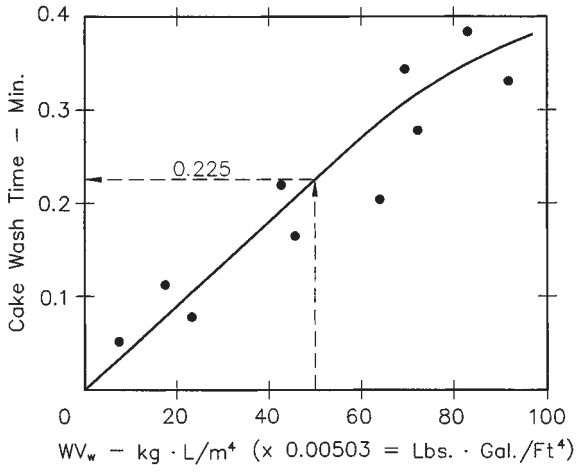


FIG. 18-104 Cake wash time correlation.

Vacuum pump capacity is conventionally based on the total cycle and expressed as $m^3/h \cdot m^2$ (cfm/ft^2) of filter area measured at pump inlet conditions. Thus, the gas volumes per unit area passing during each dry period in the cycle are totaled and divided by the cycle time to arrive at the design air rate. Since air rate measurements in the test program are based on pressure drop across the cake and filter medium only, allowance must be made for additional expansion due to pressure drop within the filter and auxiliary piping system in arriving at vacuum pump inlet conditions.

Air rate measurements made during a leaf test program account only for gas flow through the cake. An operating filter has drainage passages that must also be evacuated. The extra air flow may be conveniently accounted for in most cases by multiplying the leaf test rate by 1.10. With horizontal belt filters, one must also add for the leakage that occurs along the sliding seal and, depending upon the type of filter cloth used, edge leakage due to lateral permeability of the cloth. Typically, the total leakage can be significant, amounting to about 35 to 50 $m^3/h \cdot m^2$ (2 to 3 cfm/ft^2).

Adjustment may also be required for differences in altitude between the test site and the commercial installation. In general terms, if the plant elevation is higher, the vacuum pump size must be increased, and conversely.

Darcy's law has been used to derive an expression which reflects not only the effect of a change in elevation, but also provides a means for estimating changes in air rate resulting from changes in vacuum level and cake thickness (or cake weight per unit area). In order for this relationship to hold for changes in vacuum and cake thickness, it must be assumed that both cakes have the same specific resistance.

The generalized equation is as follows:

$$(\text{air rate})_{b2} = (\text{air rate})_{a2} \frac{(W_a)}{(W_b)} \frac{(P_{b1}^2 - P_{b2}^2)}{(P_{a1}^2 - P_{a2}^2)} \frac{(P_{a2})}{(P_{b2})} \qquad (18\text{-}66)$$

where P_1 = inlet absolute pressure
P_2 = outlet absolute pressure
a = base condition
b = revised condition
W = weight of dry cake solids/unit area/cycle

SCALE-UP FACTORS

[Purchas (ed.), *Solid/Liquid Separation Equipment Scale-Up,* Uplands Press, Croydon, England, 1977.]

The overall scale-up factor used to convert a rate calculated from bench-scale data to a design rate for a commercial installation must incorporate separate factors for each of the following:

Scale-up on rate
Scale-up on cake discharge
Scale-up on actual area

Special note should be made that these scale-up factors are *not* safety factors to allow for additional plant capacity at some future date. Their purpose is to account for differences in scale, including such things as minor deviations in the plant slurry from the sample tested, edge effects due to the size of the test equipment, close control of operating conditions during the leaf test program, and long-term medium blinding.

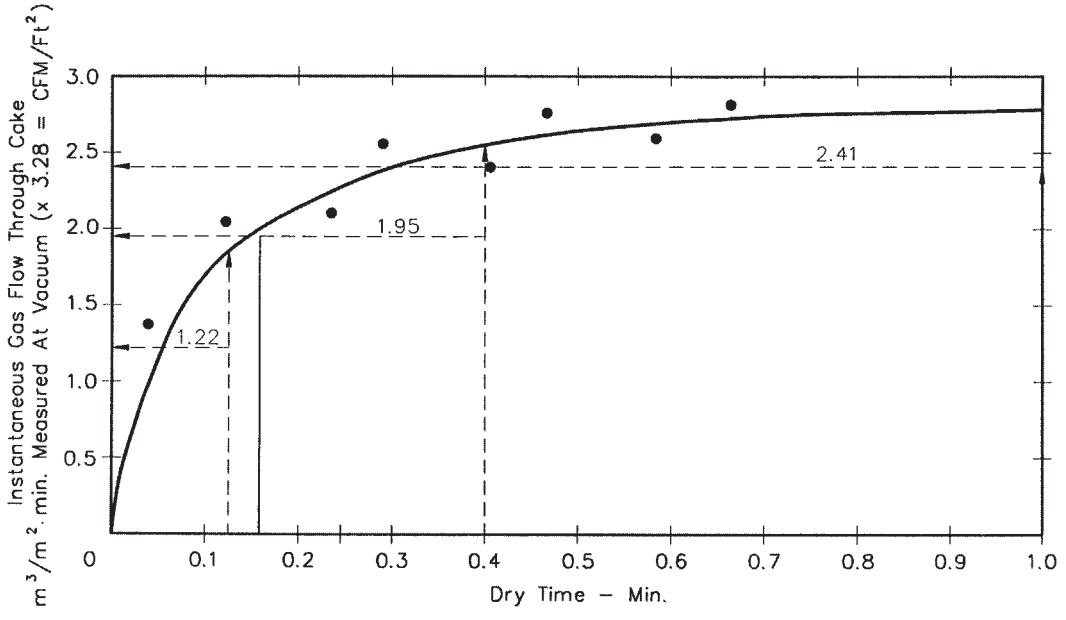


FIG. 18-105 Air flow through cake.

Scale-Up on Rate Filtration rates calculated from bench-scale data should be multiplied by a factor of 0.8 for all types of commercial units which do not employ continuous washing of the filter medium and on which there is a possibility of filter-medium blinding. For those units which employ continuous filter-medium washing, belt-type drum and horizontal units, the scale-up factor may be increased to 0.9.

The use of this scale-up factor assumes the following:
Complete cake discharge
Nominal filter area approximately equal to actual area
A representative sample
Suitable choice of filter medium
Operating conditions equal to those used in testing
Normal cloth conditioning during testing and operation

The scale-up factor on rate specifically does not allow for:
Changes in slurry filterability
Changes in feed rate
Changes in operating conditions
Cloth blinding

Where there is any doubt about some of the conditions listed above (except for cake discharge and actual area which should be handled separately) a more conservative scale-up factor should be used.

Scale-Up on Cake Discharge When a filter is selected for a particular application, it is intended that the unit be capable of discharging essentially 100 percent of the cake which is formed. There are, however, many applications which are marginal, regardless of the type of discharge mechanism used. In these cases, the experimenter must judge the percent of cake discharge to be expected and factor the design rate accordingly.

Scale-Up on Actual Area The nominal area of a filter as used by equipment manufacturers is based upon the overall dimensions of the filtering surface. The fraction of this total area that is active in filtration is a function of the filterability of the material being handled and any special treatment which the surface may receive.

The filtering surface is divided into a number of sections by division strips, radial rods, or some other impervious separator. Material which forms a thin, rather impervious cake will not form across the dividers, and thus the actual area is somewhat less than the nominal. Where relatively thick cakes of at least 1.5 cm are formed, the cake tends to form across the dividers due to cross-drainage in both the filter cake and the filter medium. In this case, the effective area is relatively close to the nominal area.

For most applications, the actual area of a drum filter will generally be no less than 94 to 97 percent of the nominal area, depending upon the size and number of sections. This variation is generally not accounted for separately and is assumed to be taken care of in the scale-up factor on filtration rate.

There are, however, certain special applications where the filter medium around the edge of the section may be deliberately blinded by painting in order to improve cake discharge. This technique is most frequently used on disk filters, with the result that the actual area may be only 75 to 85 percent of the nominal area. This is a significant deviation from the nominal area and must be considered separately.

Overall Scale-Up Factor The final design filtration rate is determined by multiplying the bench-scale filtration rate by each of the scale-up factors discussed above. While this approach may seem to be ultraconservative, one must realize that the experimenter maintains careful control over the various steps during the filter cycle while running a bench-scale test, whereas a commercial filter operates with a minimum of attendance and at average conditions which are chosen to provide a satisfactory result in a production context.

FULL-SCALE FILTER PERFORMANCE EVALUATION

The correlations which have been presented for the evaluation of bench-scale data are the same correlations which should be used to evaluate the performance of a commercial installation.

A few random samples taken from a commercial installation most probably will not provide enough insight to determine that the filter is performing as expected. However, by making use of reasonable variations in the most important parameters, the desired correlations can be developed. Bench-scale tests should be run on representative feed samples taken at the same time test runs are made on the commercial unit. The bench-scale tests can be varied over a much wider range to provide a sound basis for both the location and shape of the appropriate correlation. A comparison of these results with the data taken from the commercial installation provides a good measure for efficiency of the commercial unit and a basis for identifying problem areas on the full-scale unit.

FILTER SIZING EXAMPLES

[Purchas (ed.), *Solid/Liquid Separation Equipment Scale-Up,* Uplands Press, Croydon, England, 1977.]

The examples which follow show how data from the correlations just presented and a knowledge of the physical characteristics of a particular filter are used to determine a filtration cycle and, subsequently, the size of the filter itself. The three examples which follow involve a disk, a drum belt, and a horizontal belt filter.

Example 1: Sizing a Disk Filter Equipment physical factors, selected from Table 18-9: Maximum effective submergence = 28%; maximum portion of filter cycle available for dewatering = 45%. (High submergence versions require trunnion seals, and their use is limited to specific applications.)

Scale-up factors: On rate = 0.8; On area = 0.8; On discharge = 0.9. (Scale-up on discharge may be increased to 0.97 if based on previous experience or to 0.95 if the total filter area is based on the measured effective area of the disk.)

Objective: Determine the filter size and vacuum system capacity required to dewater 15 mtph (metric tons per hour) of dry solids and produce a cake containing an average moisture content of 25 wt %.

Calculation procedure:

1. Choose cake thickness = 1.5 cm, slightly thicker than minimum value listed in Table 18-8.
2. From Fig. 18-98, $W = 20.0$ kg dry cake/($m^2 \times$ rev.).
3. From Fig. 18-99, form time, $_f = 1.20$ min.
4. Use simplified moisture content correlating factor in Fig. 18-102.
   Choose $_d/W = 0.04$ at avg. moisture content of 25 wt %.
   Dry time = $_d = 0.04 \times 20.0 = 0.80$ min.
5. Calculate cycle time CT both on the basis of form time and dry time to determine which is controlling:
   $CT_{form} = 1.20/.28 = 4.29$ mpr (min/rev.).

TABLE 18-9 Typical Equipment Factors for Cycle Design

	% of cycle					
	Submergence		Total under active vac. or pres.	Max. for washing	Max. for dewatering only	Req'd. for cake discharge
Filter type	Apparent	Max. effective				
Drum						
Standard scraper	35	30	80	29	50–60	20
Roll discharge	35	30	80	29	50–60	20
Belt	35	30	75	29	45–50	25
Coil or string	35	30	75	29	45–50	25
Precoat	35,55	35,55	93	30	60,40	5
Horizontal belt	As req'd.	As req'd.	Lengthen as req'd.	As req'd.	As req'd.	0
Horizontal table	As req'd.	As req'd.	80	As req'd.	As req'd.	20
Tilting pan	As req'd.	As req'd.	75	As req'd.	As req'd.	25
Disk	35	28	75	None	45	25

$CT_{dry} = 0.80/.45 = 1.78$ mpr.

Therefore, cake formation rate is controlling and a cycle time of 4.29 mpr must be used.

6. Overall scale-up factor based on the factors presented previously = $0.8 \times 0.8 \times 0.9 = 0.58$

7. Design filtration rate = $(20.0/4.29)(60 \times 0.58) = 162$ kg/h × m²

8. Area required to filter 15 metric tons of dry solids per hour = $15 \times 1000/162 = 92.6$ m². The practical choice would then be the nearest commercial size of filter corresponding to this calculated area.

9. Dry time = 45% of CT = $0.45 \times 4.29 = 1.93$ min. This is a much longer dry time than required. Therefore, reduce the dry time to 1.00 min by proper bridging in the filter valve.

10. From Fig. 18-105, the average gas flow rate during the 1.00 min drying period was found by graphical integration to be 2.41 m³/m² × min.

11. Total volume of air flowing during dry period = $2.41 \times 1.00 = 2.41$ m³ per m² per cycle. Add 10% to allow for evacuation of drainage passages. Total flow = 2.65 m³/m² × cycle.

12. Required vacuum pump capacity = 2.65/4.29 = 0.62 m³/min × m² of total filter area. Allow for pressure drop within system when specifying the vacuum pump. See next example.

Example 2: Sizing a Drum Belt Filter with Washing Equipment physical factors, selected from Table 18-9: Maximum effective submergence = 30%; max. apparent subm. = 35%; max. arc for washing = 29%; portion of cycle under vacuum = 75%.

Scale-up factors: On rate = 0.9; On area = 1.0; On discharge = 1.0.

Process data: Sp. gr. of feed liquid = 1.0; TDS (total dissolved solids) in feed liquid = 4.0 wt %; fresh water used for washing; vacuum level = 18 in Hg; final cake liquid content = 25 wt %.

Objective: Determine the filter size and vacuum capacity required to dewater and wash 15 mtph of dry solids while producing a final washed cake with a moisture content of 25 wt % and containing 0.10 wt % TDS based on dry cake solids.

Calculation procedure:

1. Choose cake thickness = 0.75 cm, slightly thicker than the minimum in Table 18-8.
2. From Fig. 18-98, $W = 10$ kg/m² × cycle.
3. From Fig. 18-99, form time = 0.30 min.
4. From Fig. 18-102, $_d/W = 0.04$ for 25 wt % residual moisture.
5. Dry time = $_d = W \times 0.04 = 10.0 \times 0.04 = 0.40$ min.
6. Determine required wash quantity:
   Calculated TDS concentration in washed cake liquor:
   Liquid in final cake = $10 \times 0.25/0.75 = 3.33$ kg/m² × cycle.
   TDS in dry washed solids = $10 \times 0.001/0.999 = 0.010$ kg/m² × cycle.
   TDS in final washed cake liquor = $(0.010/3.33)100 = 0.300$ wt %.
   Percent remaining, $R = ((C_2 - C_w)/(C_1 - C_w))100$.
   Since $C_w = 0$,
   Required percent remaining, $R = (C_2/C_1)100 = (0.300/4.00)100 = 7.5\%$.
   From Fig. 18-103, required wash ratio $N = 1.35$.
   For design, add 10% → $N = 1.35 \times 1.1 = 1.49$.
   Wash vol. = $V_w = 1.49 \times 3.33/1.00 = 4.96$ L/m² × cycle.
7. Determine wash time:
   $WV_w = 10.0 \times 4.96 = 49.6$ kgL/m⁴.
   From Fig. 18-104, wash time = $_w = 0.225$ min.
8. Summary of minimum times for each operation:
   Form (step 3) = 0.30 min.
   Wash (step 6) = 0.225 min.
   Final dry (step 5) = 0.40 min.
9. Maximum washing arc = horizontal centerline to 15° past top dead center, or 29% of total cycle. Minimum percent of cycle between end of form and earliest start of wash = area between horizontal centerline and maximum apparent submergence = (50% − 35%)/2 = 7.5%.
10. Maximum percentage of cycle for wash + final dry = 75 − 30 − 7.5 = 37.5%.
11. Determine cycle time based on the rate-controlling operation:
    a. $CT_{form} = 0.30/.30 = 1.00$ mpr.
    b. $CT_{wash} = 0.225/.29 = 0.77$ mpr.
    c. $CT_{wash + dry} = (0.225 + 0.40)/.375 = 1.67$ mpr.

Therefore, the cake wash + final dry rate is controlling and a cycle time of 1.67 mpr must be used.

12. Since (*c*) is larger than (*a*) in the previous step, too thick a cake will be formed and it will not wash or dry adequately unless the effective submergence is artificially restricted to yield the design cake thickness. This may be accomplished by proper bridge-block adjustment or by vacuum regulation within the form zone of the filter valve.
13. The required washing arc of (0.225/1.67)360 = 48.5° is assumed to start at the horizontal center line. Careful control of the wash sprays will be required to minimize runback into the slurry in the vat.
14. Overall scale-up factor = $0.9 \times 1.0 \times 1.0 = 0.9$.
15. Design filtration rate = $(10.0/1.67)(60 \times 0.9)$.
    = 323.3 kg/h × m².
16. Total filter area required = $15 \times 1000/323.3 = 46.4$ m².

Nearest commercial size for a single unit could be a 10 ft dia. × 16 ft long with a total area of 502 ft² = 46.7 m².

17. Determine required vacuum capacity:
    Initial dry time = $1.67 \times 0.075 = 0.125$ min.
    Calculate gas vol. through cake using data from Fig. 18-105:
    Initial dry = $0.125 \times 1.22 = 0.153$ m³/m² × rev.
    Final dry = $0.40 \times 1.95 = 0.780$ m³/m² × rev.
    Total, including 10% for evacuation of drainage passages = $0.933 \times 1.10 = 1.03$ m³/m² × rev.

Air rate based on total cycle = 1.03/1.67 = 0.62 m³/min × m² measured at 18 in Hg vacuum.

If pressure drop through system = 1.0 in Hg and barometric pressure = 30 in Hg, design air rate = $0.62 \times 12/11 = 0.68$ m³/min × m² measured at 19 in Hg vacuum.

Horizontal Belt Filter Since the total cycle of a horizontal belt filter occurs on a single, long horizontal surface, there is no restriction with respect to the relative portions of the cycle. Otherwise, scale-up procedures are similar.

BATCH FILTRATION

Since most batch-type filters operate under pressure rather than vacuum, the following discussion will apply primarily to pressure filtration and the various types of pressure filters.

To use Eq. (18-50) one must know the pattern of the filtration process, i.e., the variation of the flow rate and pressure with time. Generally the pumping mechanism determines the filtration flow characteristics and serves as a basis for the following three categories* [Tiller and Crump, *Chem. Eng. Prog.*, **73**(10), 65 (1977)]:

1. *Constant-pressure filtration.* The actuating mechanism is compressed gas maintained at a constant pressure.
2. *Constant-rate filtration.* Positive-displacement pumps of various types are employed.
3. *Variable-pressure, variable-rate filtration.* The use of a centrifugal pump results in this pattern: the discharge rate decreases with increasing back pressure.

Flow rate and pressure behavior for the three types of filtration are shown in Fig. 18-106. Depending on the characteristics of the centrifugal pump, widely differing curves may be encountered, as suggested by the figure.

Constant-Pressure Filtration For constant-pressure filtration Eq. (18-51) can be integrated to give the following relationships between total time and filtrate measurements:

$$\frac{\theta}{V/A} = \frac{\mu\alpha}{2P}\frac{W}{A} + \frac{\mu r}{P} \tag{18-67}$$

$$\frac{\theta}{V/A} = \frac{\mu\alpha w}{2P}\frac{V}{A} + \frac{\mu r}{P} \tag{18-68}$$

$$\frac{\theta}{V/A} = \frac{\mu\alpha\rho c}{2P(1-mc)}\frac{V}{A} + \frac{\mu r}{P} \tag{18-69}$$

For a given constant-pressure filtration, these may be simplified to

$$\frac{\theta}{V/A} = K_p\frac{W}{A} + C = K'_p\frac{V}{A} + C \tag{18-70}$$

where K_p, K'_p, and C are constants for the conditions employed. It should be noted that K_p, K'_p, and C depend on filtering pressure not only in the obvious explicit way but also in the implicit sense that α, m, and r are generally dependent on P.

Constant-Rate Filtration For substantially incompressible cakes, Eq. (18-51) may be integrated for a constant rate of slurry feed to the filter to give the following equations, in which filter-medium resistance is treated as the equivalent constant-pressure component to be deducted from the rising total pressure drop to

* A combination of category 2 followed by category 1 as parts of the same filtration cycle is considered by some as a fourth category. For a method of combining the constant-rate and constant-pressure equations for such a cycle, see Brown, loc. cit.

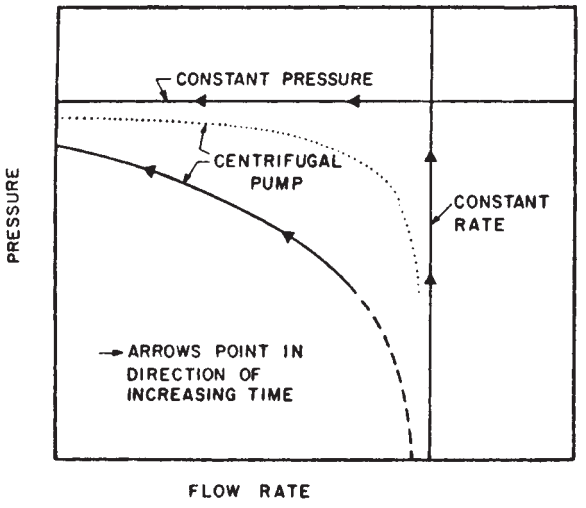


FIG. 18-106 Typical filtration cycles. [*Tiller and Crump,* Chem. Eng. Prog. *73(10), 72(1977), by permission.*]

give the variable pressure through the filter cake [Ruth, *Ind. Eng. Chem.,* **27,** 717 (1935)]:

$$\frac{\theta}{V/A} = \frac{1}{\text{rate per unit area}} = \frac{\mu\alpha}{P - P_1}\frac{W}{A} \tag{18-71}$$

which may also be written

$$\frac{\theta}{V/A} = \frac{\mu\alpha w}{P - P_1}\frac{V}{A} = \frac{\mu\alpha\rho c}{(P - P_1)(1 - mc)}\frac{V}{A} \tag{18-72}$$

In these equations P_1 is the pressure drop through the filter medium.

$$P_1 = \mu r(V/A\theta)$$

For a given constant-rate run, the equations may be simplified to

$$V/A = P/K_r + C' \tag{18-73}$$

where K_r and C' are constants for the given conditions.

Variable-Pressure, Variable-Rate Filtration The pattern of this category complicates the use of the basic rate equation. The method of Tiller and Crump (loc. cit.) can be used to integrate the equation when the characteristic curve of the feed pump is available.

In the filtration of small amounts of fine particles from liquid by means of bulky filter media (such as absorbent cotton or felt) it has been found that the preceding equations based upon the resistance of a cake of solids do not hold, since no cake is formed. For these cases, in which filtration takes place on the surface or within the interstices of a medium, analogous equations have been developed [Hermans and Bredée, *J. Soc. Chem. Ind.,* **55T,** 1 (1936)]. These are usefully summarized, for both constant-pressure and constant-rate conditions, by Grace [*Am. Inst. Chem. Eng. J.,* **2,** 323 (1956)]. These equations often apply to the clarification of such materials as sugar solutions, viscose and other spinning solutions, and film-casting dopes.

If a **constant-pressure test** is run on a slurry, care being taken that not only the pressure but also the temperature and the solid content remain constant throughout the run and that time readings begin at the exact start of filtration, one can observe values of filtrate volume or weight and corresponding elapsed time. With the use of the known filtering area, values of $\theta/(V/A)$ can be calculated for various values of V/A which, when plotted with $\theta/(V/A)$ as the ordinate and V/A as the abscissa (Fig. 18-107*a*), result in a straight line having the slope $\mu\alpha w/2P$ and an intercept on the vertical axis of $\mu r/P$. Since μ, w, and P are known, α and r can be calculated from

$$\alpha = 2P/\mu w \times (\text{slope})$$

and

$$r = P/\mu \times (\text{vertical intercept})$$

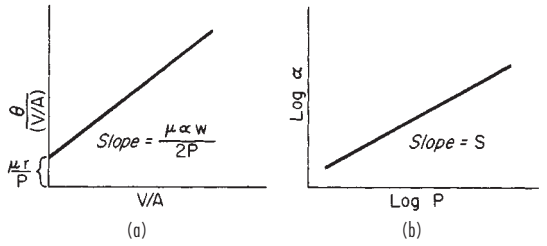


FIG. 18-107 Typical plots of filtration data.

The effect of the change of any variable not affecting α or r can now be estimated. It should be remembered that α and r usually depend on P and may be affected by w.

The symbol α represents the average specific cake resistance, which is a constant for the particular cake in its immediate condition. In the usual range of operating conditions it is related to the pressure by the expression

$$\alpha = \alpha' P^s \tag{18-74}$$

where α' is a constant determined largely by the size of the particles forming the cake; s is the cake compressibility, varying from 0 for rigid, incompressible cakes, such as fine sand and diatomite, to 1.0 for very highly compressible cakes. For most industrial slurries, s lies between 0.1 and 0.8. The symbol r represents the resistance of unit area of filter medium but includes other losses (besides those across the cake and the medium) in the system across which P is the pressure drop.

It should be noted also that the intercept is difficult to determine accurately because of large potential experimental error in observing the time of the start of filtration and the time-volume correspondence during the first moments when the filtration rate is high. The value of r calculated from the intercept may vary appreciably from test to test, and will almost always be different from the value measured with clean medium in a permeability test.

To determine the effect of a change in pressure, it is necessary to run tests at three or more pressures, preferably spanning the range of interest. Plotting α or r against P on log-log paper (or log α or log r against the log P on cartesian coordinates) results in an approximate straight line (Fig. 18-107*b*) from which one may estimate values of α or r at interpolated or reasonably extrapolated magnitudes of P. The slope of the line is the index of a power relationship between α and P or r and P.

Not uncommonly r is found to be only slightly dependent on pressure. When this is true and especially when the filter-medium resistance is, as it should be, relatively small, an average value may be used for all pressures.

It is advisable to start a constant-pressure filtration test, like a comparable plant operation, at a low pressure, and smoothly increase the pressure to the desired operating level. In such cases, time and filtrate-quantity data should not be taken until the constant operating pressure is realized. The value of r calculated from the extrapolated intercept then reflects the resistance of both the filter medium and that part of the cake deposited during the pressure-buildup period. When only the total mass of dry cake is measured for the total cycle time, as is usually true in vacuum leaf tests, at least three runs of different lengths should be made to permit a reliable plot of θ/V against W. If rectification of the resulting three points is dubious, additional runs should be made.

Pressure Tests

Leaf Tests A bomb filter is used for small-scale leaf tests to simulate the performance of pressure-leaf (leaf-in-shell) filters. The equipment used is a small [50.8- by 50.8-mm (2- by 2-in)] leaf, covered with appropriate filter medium, suspended in a cell large enough to contain sufficient slurry to form the desired cake (Fig. 18-108). The slurry may be agitated gently, for example, by an air sparger.

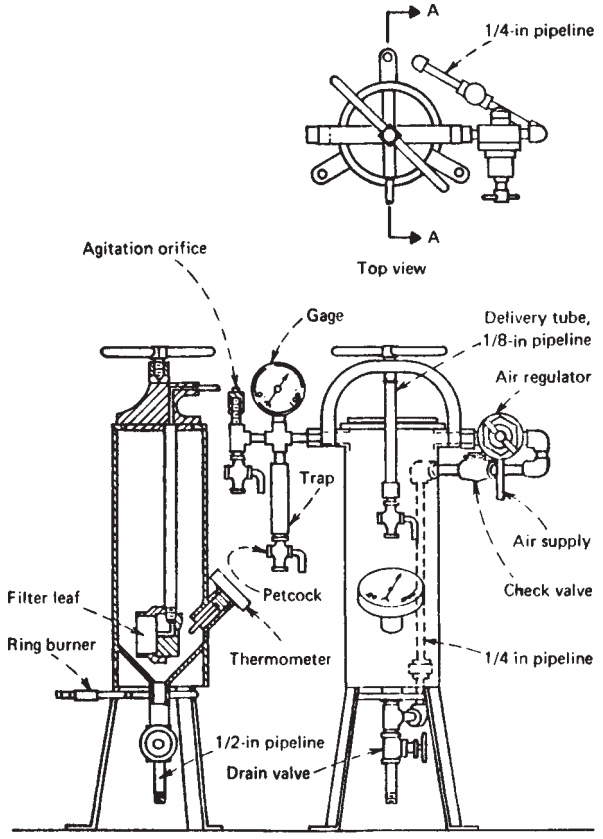


FIG. 18-108 Bomb filter for small-scale pressure filtration tests. [*Silverblatt et al.,* Chem. Eng., ***81****(9), 132 (1974), by permission.*]

Although incremental time and filtrate volume may be taken during a cake-forming cycle at a selected pressure to permit a plot like Fig. 18-107*a* from a single run, it may be more satisfactory to make several successive quick runs at the same pressure but for different lengths of time, recording only the terminal values of filtrate volume, time, and cake mass. Operation of the commercial unit should be kept in mind when the test cycles are planned. Displacement washing and air blowing of the cake should be tried if appropriate. Wet discharge can be simulated by opening the cell and playing a jet of water on the cake; dry discharge, by applying a gentle air blast to the filtrate-discharge tube. Tests at several pressures must be conducted to determine the compressibility of the cake solids.

Plate-and-Frame Tests These tests should be conducted if the use of a filter press in the plant is anticipated; at least a few confirming tests are advisable after preliminary leaf tests, unless the slurry is very rapidly filtering. A laboratory-size filter press consisting of two plates and a single frame may be used. It will permit the observation of solids-settling, cake-packing, and washing behavior, which may be quite different for a frame than for a leaf.

Compression-Permeability Tests Instead of model leaf tests, compression-permeability experiments may be substituted with advantage for appreciably compressible solids. As in the case of constant-rate filtration, a single run provides data equivalent to those obtained from a series of constant-pressure runs, but it avoids the data-treatment complexity of constant-rate tests.

The equipment consists of a cylindrical cell with a permeable bottom and an open top, into which is fitted a close-clearance, hollow, cylindrical piston with a permeable bottom. Slurry is poured into the cell, and a cake is formed by applying gentle vacuum to the filtrate discharge line. The cell is then filled with filtrate, and the counterweighted piston is allowed to descend to the cake level. Successive increments of mechanical stress are applied to the solids, at each of which the permeability of the cake is determined by passing filtrate through the piston under low head.

The experimental procedure and method of treatment of compression-permeability data have been explained by Grace [*Chem. Eng. Prog.,* **49,** 303, 427 (1953)], who showed that the values of α measured in such a cell and in a pressure filter were the same, and by Tiller [*Filtr. Sep.,* **12,** 386 (1975)].

Scaling Up Test Results The results of small-scale tests are determined as dry weight of solids or volume of filtrate per unit of area per cycle. This quantity multiplied by the number of cycles per day permits the calculation of either the filter area required for a stipulated daily capacity or the daily capacity of a specified plant filter. The scaled-up filtration area should be increased by 25 percent as a factor of uncertainty. In the calculation of cycle length, proper account must be made of the downtime of a batch filter.

FILTER MEDIA

All filters require a filter medium to retain solids, whether the filter is for cake filtration or for filter-medium or depth filtration. Specification of a medium is based on retention of some minimum particle size at good removal efficiency and on acceptable life of the medium in the environment of the filter. The selection of the type of filter medium is often the most important decision in success of the operation. For cake filtration, medium selection involves an optimization of the following factors:

1. Ability to bridge solids across its pores quickly after the feed is started (i.e., minimum propensity to bleed)
2. Low rate of entrapment of solids within its interstices (i.e., minimum propensity to blind)
3. Minimum resistance to filtrate flow (i.e., high production rate)
4. Resistance to chemical attack
5. Sufficient strength to support the filtering pressure
6. Acceptable resistance to mechanical wear
7. Ability to discharge cake easily and cleanly
8. Ability to conform mechanically to the kind of filter with which it will be used
9. Minimum cost

For filter-medium filtration, attributes 3, 4, 5, 8, and 9 of the preceding list apply and must have added to them (*a*) ability to retain the solids required, (*b*) freedom from discharge of lint or other adulterant into the filtrate, and (*c*) ability to plug slowly (i.e., long life).

Filter-medium selection embraces many types of construction: fabrics of woven fibers, felts, and nonwoven fibers, porous or sintered solids, polymer membranes, or particulate solids in the form of a permeable bed. Media of all types are available in a wide choice of materials.

Fabrics of Woven Fibers For cake filtration these fabrics are the most common type of medium. A wide variety of materials are available; some popular examples are listed in Table 18-10, with ratings for chemical and temperature resistance. In addition to the material of the fibers, a number of construction characteristics describe the filter cloth: (1) weave, (2) style number, (3) weight, (4) count, (5) ply, and (6) yarn number. Of the many types of weaves available, only four are extensively used as filter media: plain (square) weave, twill, chain weave, and satin.

All these weaves may be made from any textile fiber, natural or synthetic. They may be woven from spun staple yarns, multifilament continuous yarns, or monofilament yarns. The performance of the filter cloth depends on the weave and the type of yarn.

A recently developed medium known as a **double weave** incorporates different yarns in warp and fill in order to combine the specific advantages of each type. An example of this is Style 99FS, made by SCAPA Filtration (formerly P&S Filtration), in which multifilament warp yarns provide good cake release properties and spun staple fill yarns contribute to greater retentivity.

Metal Fabrics or Screens These are available in several types of weave in nickel, copper, brass, bronze, aluminum, steel, stainless steel, Monel, and other alloys. In the plain weave, 400 mesh is the closest

TABLE 18-10 Characteristics of Filter-Fabric Materials*

Generic name and description	Breaking tenacity, g/denier	Abrasion resistance	Resistance to acids	Resistance to alkalies	Resistance to oxidizing agents	Resistance to solvents	Specific gravity	Maximum operating temperature, °F†
Acetate—cellulose acetate. When not less than 92% of the hydroxyl groups are acetylated, "triacetate" may be used as a generic description.	1.2–1.5	G	F	P	G	G	1.33	210
Acrylic—any long-chain synthetic polymer composed of at least 85% by weight of acrylonitrile units.	2.0–4.8	G	G	F	G	E	1.18	300
Glass—fiber-forming substance is glass.	3.0–7.2	P	E	P	E	E	2.54	600
Metallic—composed of metal, metal-coated plastic, plastic-coated metal, or a core completely covered by metal.	—	G						
Modacrylic—fiber-forming substance is any long-chain synthetic polymer composed of less than 85% but at least 35% by weight of acrylonitrile units.	2.5–3.0	G	G	G	G	G	1.30	180
Nylon—any long-chain synthetic polyamide having recurring amide groups as an integral part of the polymer chain.	3.8–9.2	E	F–P	G	F–P	G	1.14	225
Polyester—any long-chain synthetic polymer composed of at least 85% by weight of an ester of a dihydric alcohol and terephthalic acid (*p*—HOOC—C_6H_4—COOH).	2.2–7.8	E–G	G	G–F	G	G	1.38	300
Polyethylene—long-chain synthetic polymer composed of at least 85% weight of ethylene.	1.0–7.0	G	G	G	F	G	0.92	165‡
Polypropylene—long-chain synthetic polymer composed of at least 85% by weight of propylene.	4.8–8.5	G	E	E	G	G	0.90	250§
Cotton—natural fibers.	3.3–6.4	G	P	F	G	E–G	1.55	210
Fluorocarbon—long-chain synthetic polymer composed of tetrafluoroethylene units.	1.0–2.0	F	E	E	E	G	2.30	550¶

*Adapted from Mais, *Chem. Eng.*, **78**(4), 51 (1971). Symbols have the following meaning: E = excellent, G = good, F = fair, P = poor.
†°C = (°F − 32)/1.8; K = (°F + 459.7)/1.8.
‡Low-density polymer. Up to 230°F for high-density.
§Heat-set fabric; otherwise lower.
¶Requires ventilation because of release of toxic gases above 400°F.

wire spacing available, thus limiting use to coarse crystalline slurries, pulps, and the like. The "Dutch weaves" employing relatively large, widely spaced, straight warp wires and relatively small crimped filling wires can be woven much more closely, providing a good medium for filtering fine crystals and pulps. This type of weave tends to plug readily when soft or amorphous particles are filtered and makes the use of filter aid desirable. Good corrosion and high temperature resistance of properly selected metals makes filtrations with metal media desirable for long-life applications. This is attractive for handling toxic materials in closed filters to which minimum exposure by maintenance personnel is desirable.

Pressed Felts and Cotton Batting These materials are used to filter gelatinous particles from paints, spinning solutions, and other viscous liquids. Filtration occurs by deposition of the particles in and on the fibers throughout the mat.

Nonwoven media consist of web or sheet structures which are composed primarily of fibers or filaments bonded together by thermal, chemical, or mechanical (such as needlepunching) means. Needled felts are the most commonly used nonwoven fabric for liquid filtration. Additional strength often is provided by including a scrim of woven fabric encapsulated within the nonwoven material. The surface of the medium can be calendered to improve particle retention and assist in filter cake release. Weights range from 270 to 2700 gm/m^2 (8 to 80 oz/yd^2). Because of their good retentivity, high strength, moderate cost, and resistance to blinding, nonwoven media have found wide acceptance in filter press use, particularly in mineral concentrate filtration applications. They are used frequently on horizontal belt filters where their dimensional stability reduces or eliminates wrinkling and biasing problems often encountered with woven belts.

Filter Papers These papers come in a wide range of permeability, thickness, and strength. As a class of material, they have low strength, however, and require a perforated backup plate for support.

Rigid Porous Media These are available in sheets or plates and tubes. Materials used include sintered stainless steel and other metals, graphite, aluminum oxide, silica, porcelain, and some plastics—a gamut that allows a wide range of chemical and temperature resistance. Most applications are for clarification.

Polymer Membranes These are used in filtration applications for fine-particle separations such as microfiltration and ultrafiltration (clarification involving the removal of 1-μm and smaller particles). The membranes are made from a variety of materials, the commonest being cellulose acetates and polyamides. Membrane filtration, discussed in Sec. 22, has been well covered by Porter (in Schweitzer, op. cit., sec. 2.1).

Media made from woven or nonwoven fabrics coated with a polymeric film, such as Primapor, made by SCAPA Filtration, and Gore-Tex, made by W. L. Gore and Associates, combine the high retentivity characteristics of a membrane with the strength and durability of a thick filter cloth. These media are used on both continuous and batch filters where excellent filtrate clarity is required.

Granular Beds of Particulate Solids Beds of solids like sand or coal are used as filter media to clarify water or chemical solutions containing small quantities of suspended particles. Filter-grade grains of desired particle size can be purchased. Frequently beds will be constructed of layers of different materials and different particle sizes.

Various types of filter media and the materials of which they are constructed are surveyed extensively by Purchas (*Industrial Filtration of Liquids,* CRC Press, Cleveland, 1967, chap. 3), and characterizing measurements (e.g., pore size, permeability) are reviewed in detail by Rushton and Griffiths (in Orr, op. cit., chap. 3). Briefer summaries of classification of media and of practical criteria for the selection of a filter medium are presented by Shoemaker (op. cit., p. 26) and Purchas [*Filtr. Sep.,* **17,** 253, 372 (1980)].

FILTER AIDS

Use of filter aids is a technique frequently applied for filtrations in which problems of slow filtration rate, rapid medium blinding, or unsatisfactory filtrate clarity arise. Filter aids are granular or fibrous solids capable of forming a highly permeable filter cake in which very fine solids or slimy, deformable flocs may be trapped. Application of filter aids may allow the use of a much more permeable filter medium than the clarification would require to produce filtrate of the same quality by depth filtration.

Filter aids should have low bulk density to minimize settling and aid good distribution on a filter-medium surface that may not be horizontal. They should also be porous and capable of forming a porous cake to minimize flow resistance, and they must be chemically inert to the filtrate. These characteristics are all found in the two most popular commercial filter aids: diatomaceous silica (also called diatomite, or diatomaceous earth), which is an almost pure silica prepared from deposits of diatom skeletons; and expanded perlite, particles of "puffed" lava that are principally aluminum alkali silicate. Cellulosic fibers (ground wood pulp) are sometimes used when siliceous materials cannot be used but are much more compressible. The use of other less effective aids (e.g., carbon and gypsum) may be justified in special cases. Sometimes a combination of carbon and diatomaceous silica permits adsorption in addition to filter-aid performance. Various other materials, such as salt, fine sand, starch, and precipitated calcium carbonate, are employed in specific industries where they represent either waste material or inexpensive alternatives to conventional filter aids.

Diatomaceous Silica Filter aids of diatomaceous silica have a dry bulk density of 128 to 320 kg/m^3 (8 to 20 lb/ft^3), contain particles mostly smaller than 50 μm, and produce a cake with porosity in the range of 0.9 (volume of voids/total filter-cake volume). The high porosity (compared with a porosity of 0.38 for randomly packed uniform spheres and 0.2 to 0.3 for a typical filter cake) is indicative of its filter-aid ability. Different methods of processing the crude diatomite result in a series of filter aids having a wide range of permeability.

Perlite Perlite filter aids are somewhat lower in bulk density (48 to 96 kg/m^3, or 3 to 6 lb/ft^3) than diatomaceous silica and contain a higher fraction of particles in the 50- to 150-μm range. Perlite is also available in a number of grades of differing permeability and cost, the grades being roughly comparable to those of diatomaceous silica. Diatomaceous silica will withstand slightly more extreme pH levels than perlite, and it is said to be somewhat less compressible.

Filter aids are used in two ways: (1) as a precoat and (2) mixed with the slurry as a "body feed." Precoat filtration, employing a thin layer of about 0.5 to 1.0 kg/m^2 (0.1 to 0.2 lb/ft^2) deposited on the filter medium prior to beginning feed to the filter, is in wide use to protect the filter medium from fouling by trapping solids before they reach the medium. It also provides a finer matrix to trap fine solids and assure filtrate clarity. Body-feed application is the continuous addition of filter aid to the filter feed to increase the porosity of the cake. The amount of addition must be determined by trial, but in general, the quantity added should at least equal the amount of solids to be removed. For solids loadings greater than 1000 ppm this may become a significant cost factor. An acceptable alternative might be to use a rotary vacuum precoat filter [Smith, *Chem. Eng.,* **83**(4), 84 (1976)]. Further details of filter-aid filtration are set forth by Cain (in Schweitzer, op. cit., sec. 4.2) and Hutto [*Am. Inst. Chem. Eng. Symp. Ser.,* **73**(171), 50 (1977)]. Figure 18-109 shows a flow sheet indicating arrangements for both precoat and body-feed applications. Most filter aid is used on a one-time basis, although some techniques have been demonstrated to reuse precoat filter aid on vertical-tube pressure filters.

FILTRATION EQUIPMENT

Cake Filters Filters that accumulate appreciable visible quantities of solids on the surface of a filter medium are called cake filters. The slurry feed may have a solids concentration from about 1 percent to greater than 40 percent. The filter medium on which the cake forms is relatively open to minimize flow resistance, since once the cake forms, it becomes the effective filter medium. The initial filtrate therefore may contain unacceptable solids concentration until the cake is formed. This situation may be made tolerable by recycling the filtrate until acceptable clarity is obtained or by using a downstream polishing filter (clarifying type).

Cake filters are used when the desired product of the operation is the solids, the filtrate, or both. When the filtrate is the product, the degree of removal from the cake by washing or blowing with air or gas becomes an economic optimization. When the cake is the desired product, the incentive is to obtain the desired degree of cake purity by washing, blowing, and sometimes mechanical expression of residual liquid.

Implicit in cake filtration is the removal and handling of solids, since the cake is usually relatively dry and compacted. Cakes can be sticky and difficult to handle; therefore, the ability of a filter to discharge the cake cleanly is an important equipment-selection criterion.

In the operational sense, some filters are batch devices, whereas others are continuous. This difference provides the principal basis for classifying cake filters in the discussion that follows. The driving force by which the filter functions—hydrostatic head ("gravity"), pressure imposed by a pump or a gas blanket, or atmospheric pressure ("vacuum")—will be used as a secondary criterion.

Batch Cake Filters

Nutsche Filters A nutsche is one of the simplest batch filters. It is a tank with a false bottom, perforated or porous, which may either support a filter medium or act as the filter medium. The slurry is fed into the filter vessel, and separation occurs by gravity flow, gas pressure, vacuum, or a combination of these forces. The term "nutsche" comes from the German term for sucking, and vacuum is the common operating mode.

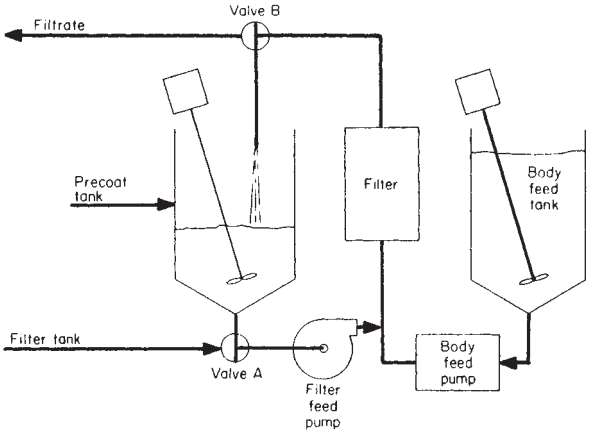


FIG. 18-109 Filter-aid filtration system for precoat or body feed. (*Schweitzer,* Handbook of Separation Techniques for Chemical Engineers, *p. 4-12. Copyright 1979 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Company.*)

The design of most nutsche filters is very simple, and they are often fabricated by the user at low cost. The filter is very frequently used in laboratory, pilot-plant, or small-plant operation. For large-scale processing, however, the excessive floor area encumbered per unit of filtration area and the awkwardness of cake removal are strong deterrents. For small-scale operations, cake is manually removed. For large-scale applications, cake may be further processed by reslurrying or redissolving; or it may be removed manually (by shovel) or by mechanical discharge arrangements such as a movable filter medium belt.

Thorough displacement washing is possible in a nutsche if the wash solvent is added before the cake begins to be exposed to air displacement of filtrate. If washing needs to be more effective, an agitator can be provided in the nutsche vessel to reslurry the cake to allow adequate diffusion of solute from the solids.

Horizontal Plate Filter The horizontal multiple-plate pressure filter consists of a number of horizontal circular drainage plates and guides placed in a stack in a cylindrical shell (Fig. 18-110). In normal practice the filtering pressure is limited to 345 kPa (50 psig), although special filters have been designed for shell pressures of 2.1 MPa (300 psig) or higher.

Filter Press The filter press, one of the most frequently used filters in the early years of the chemical industry, is still widely employed. Often referred to generically (in error) as the plate-and-frame filter, it has probably over 100 design variations. Two basic popular designs are the flush-plate, or plate-and-frame, design and the recessed-plate press. Both are available in a wide range of materials: metals, coated metals, plastics, or wood.

Plate-and-frame press. This press is an alternate assembly of plates covered on both sides with a filter medium, usually a cloth, and hollow frames that provide space for cake accumulation during filtration. The frames have feed and wash manifold ports, while the plates have filtrate drainage ports. The plates and frames usually are rectangular, although circles and other shapes also are used (Fig. 18-111). They are hung on a pair of horizontal support bars and pressed together during filtration to form a watertight closure between two end plates, one of which is stationary. The press may be closed manually, hydraulically, or by a motor drive. Several feed and filtrate discharge arrangements are possible. In the most popular, the feed and discharge of the several elements of the press are manifolded via some of the holes that are in the four corners of each plate and frame (and filter cloth) to form continuous longitudinal channels from the stationary end plate to the other end of the press. Alternatively, the filtrate may be drained from each plate by an individual valve and spigot (for open discharge) or tubing (for closed). Top feed to and bottom discharge from the chambers provide maximum recovery of filtrate and maximum mean cake dryness. This arrangement is especially suitable for heavy fast-settling solids. For most slurries, bottom feed and top filtrate discharge allow quick air displacement and produce a more uniform cake.

Two wash techniques are used in plate-and-frame filter presses, illustrated in Fig. 18-112. In simple washing, the wash liquor follows the same path as the filtrate. If the cake is not extremely uniform and highly permeable, this type of washing is ineffective in a well-filled press. A better technique is thorough washing, in which the wash is introduced to the faces of alternate plates (with their discharge channels valved off). The wash passes through the entire cake and exits through the faces of the other plates. This improved technique requires a special design and the assembly of the plates in proper order. Thorough washing should be used only when the frames are well filled, since an incomplete fill of cake will allow cake collapse during the wash entry. The remainder of the wash flow will bypass through cracks or channels opened in the cake.

Filter presses are made in plate sizes from 10 by 10 cm (4 by 4 in) to 1.5 by 1.8 m (61 by 71 in). Frame thickness ranges from 0.3 to 20 cm (0.125 to 8 in). Operating pressures up to 689 kPa (100 psig) are common, with some presses designed for 6.9 MPa (1000 psig). Some metal units have cored plates for steam or refrigerant. Maximum pressure for wood or plastic frames is 410 to 480 kPa (60 to 70 psig).

The filter press has the advantage of simplicity, low capital cost, flexibility, and ability to operate at high pressure in either a cake-filter or a clarifying-filter application. Floor-space and headroom needs per unit of filter area are small, and capacity can be adjusted by adding or removing plates and frames. Filter presses are cleaned easily, and the filter medium is easily replaced. With proper operation a denser, drier cake compared with that of most other filters is obtained.

There are several serious disadvantages, including imperfect washing due to variable cake density, relatively short filter-cloth life due to the mechanical wear of emptying and cleaning the press (often involving scraping the cloth), and high labor requirements. Presses frequently drip or leak and thereby create housekeeping problems, but the biggest problem arises from the requirement to open the filter for cake discharge. The operator is thus exposed routinely to the contents of the filter, and this is becoming an increasingly severe disadvantage as more and more materials once believed safe are given restricted exposure limits.

Recessed-plate filter press. This press is similar to the plate-and-frame press in appearance but consists only of plates (Fig. 18-113).

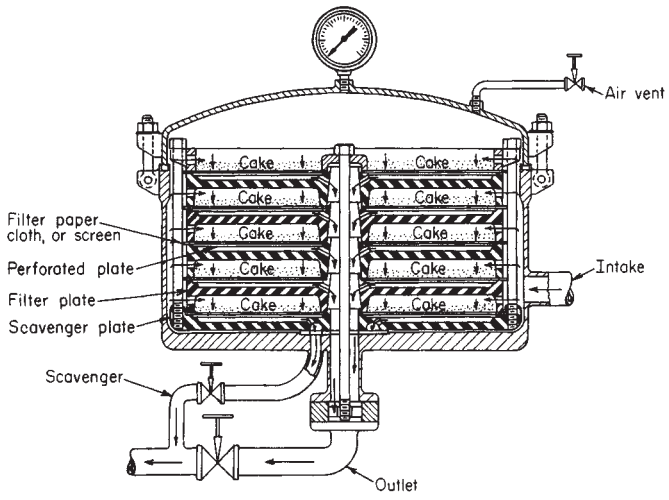


FIG. 18-110 Elevation section of a Sparkler horizontal plate filter. (*Sparkler Filters, Inc.*)

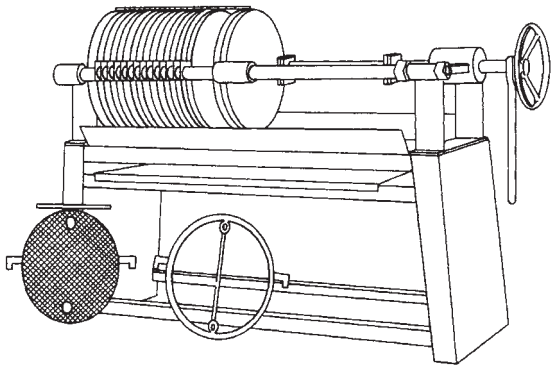


FIG. 18-111 Circular-plate fabricated-metal filter press. (*Star Systems Filtration Division.*)

Both faces of each plate are hollowed to form a chamber for cake accumulation between adjacent plates. This design has the advantage of about half as many joints as a plate-and-frame press, making a tight closure more certain. Figure 18-114 shows some of the features of one type of recessed-plate filter which has a gasket to further minimize leaks. Air can be introduced behind the cloth on both sides of each plate to assist cake removal.

Some interesting variations of standard designs include the ability to roll the filter to change from a bottom to a top inlet or outlet and the ability to add blank dividers to convert a press to a multistage press for further clarification of the filtrate or to do two separate filtrations simultaneously in the same press. Some designs have rubber membranes between plates which can be expanded when filtration is finished to squeeze out additional moisture. Some designs feature automated opening and cake-discharge operations to reduce labor requirements. Examples of this type of pressure filter include Larox, Vertipress, and Oberlin.

Internal Cake Tube Filters or Liquid Bag Filters This type of filter, such as manufactured by Industrial Filter and Pump Mfg. Co., Rosedale, Illinois, and many others, utilizes one or more perforated tubes supported by a tube sheet or by the lip of the pressure vessel. A cylindrical filter bag sealed at one end is inserted into the perforated tube. The open end of the filter bag generally has a flange or special seal ring to prevent leakage.

Slurry under pressure is admitted to the chamber between the head of the shell and the tube sheet, whence it enters and fills the tubes. Filtration occurs as the filtrate passes radially outward through the filter medium and the wall of each tube into the shell and on out the filtrate discharge line, depositing cake on the medium. The filtration cycle is ended when the tubes have filled with cake or when the media have become plugged. The cake can be washed (if it has not been allowed to fill the tubes completely) and air-blown. The filter has a removable head to provide easy access to the tube sheet and mouth of the tubes; thus "sausages" of cake can be removed by taking out the filter bags or each tube and bag assembly together. The tubes themselves are easily removed for inspection and cleaning.

The advantages of the tubular filter are that it uses an easily replaced filter medium, its filtration cycle can be interrupted and the shell can be emptied of prefilt at any time without loss of the cake, the cake is readily recoverable in dry form, and the inside of the filter is conveniently accessible. There is also no unfiltered heel. Disadvantages are the necessity and attendant labor requirements of emptying by hand and replacing the filter media and the tendency for heavy solids to settle out in the header chamber. Applications are as a scavenger filter to remove fines not removed in a prior-filtration stage with a different kind of equipment, to handle the runoff from other filters, and in semiworks and small-plant operations in which the filter's size, versatility, and cleanliness recommend it.

External-Cake Tubular Filters Several filter designs are available with vertical tubes supported by a filtrate-chamber tube sheet in a vertical cylindrical vessel (Fig. 18-115). The tubes may be made of wire cloth; porous ceramic, carbon, plastic, or metal; or closely wound wire. The tubes may have a filter cloth on the outside. Frequently a filter-aid precoat will be applied to the tubes. The prefilt slurry is fed near the bottom of the vertical vessel. The filtrate passes from the outside to the inside of the tubes and into a filtrate chamber at the top or the bottom of the vessel. The solids form a cake on the outside of the tubes with the filter area actually increasing as the cake builds up, partially compensating for the increased flow resistance of the thicker cake. The filtration cycle continues until the differential pressure reaches a specified level, or until about 25 mm (1 in) of cake thickness is obtained.

Cake-discharge methods are the chief distinguishing feature among the various designs. That of the Industrial Filter & Pump Hydro-Shoc, for example, removes cake from the tubes by filtrate backflushing assisted by the "shocking" action of a compressed-gas pocket formed

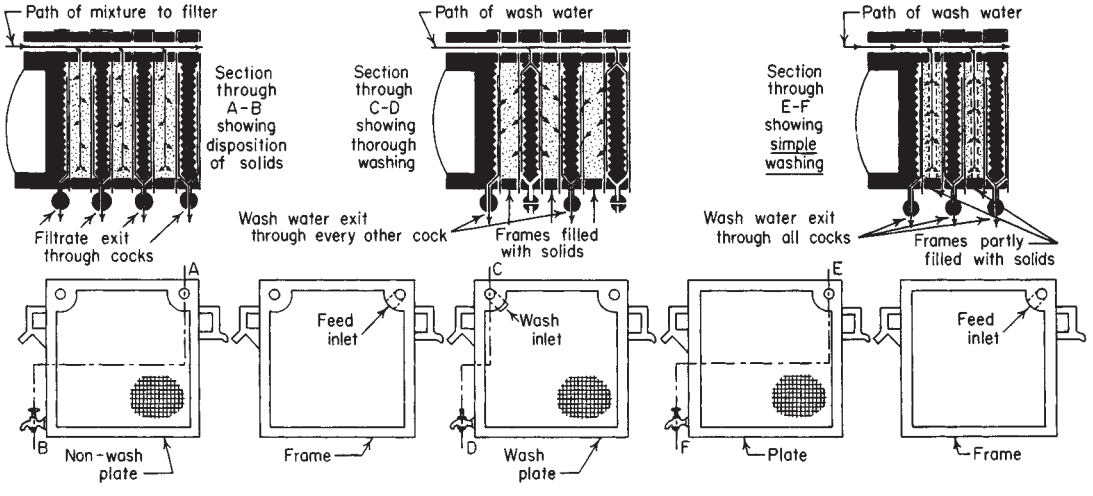


FIG. 18-112 Filling and washing flow patterns in a filter press. (*D. R. Sperry & Co.*)

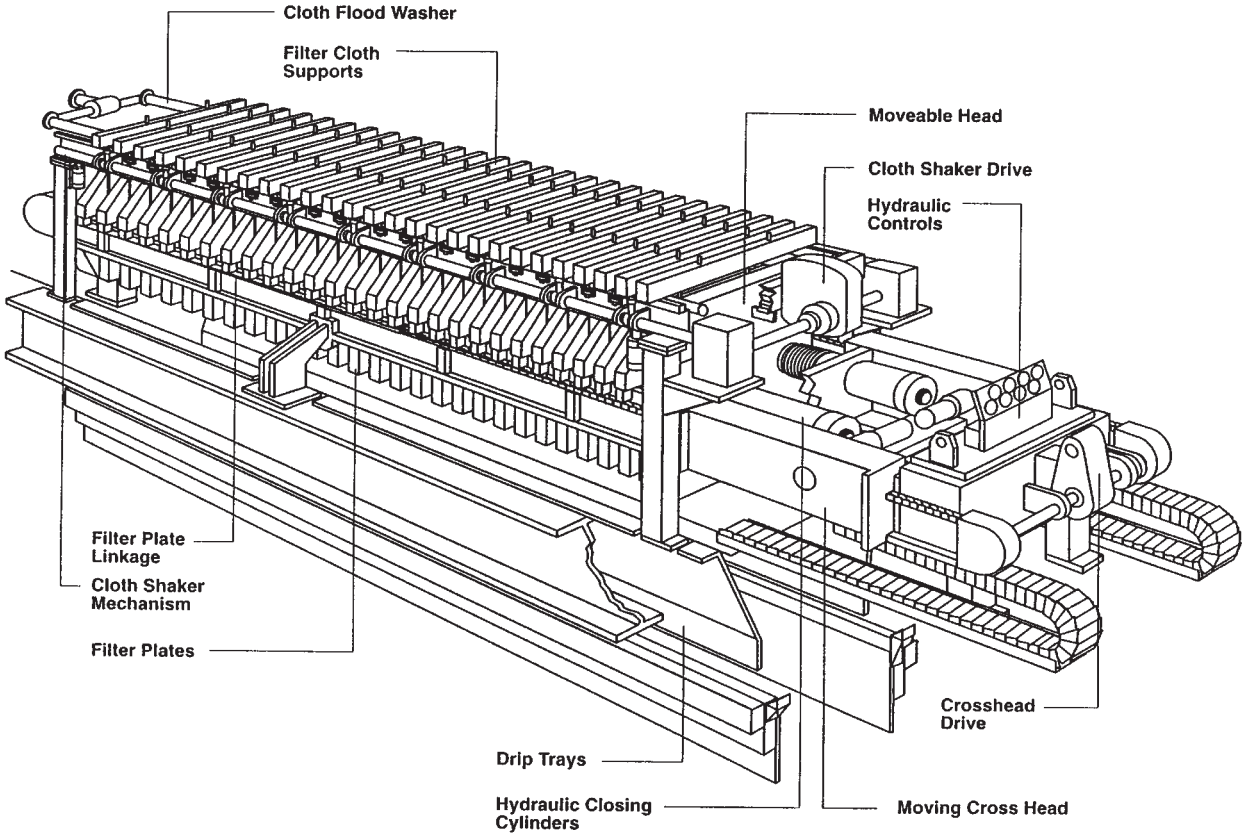


FIG. 18-113 Automated recessed-plate filter press used in mineral applications. (*EIMCO Process Equipment Co.*)

in the filtrate chamber at the top of the vertical vessel. Closing the filtrate outlet valve while continuing to feed the filter causes compression of the gas volume trapped in the dome of the vessel until, at the desired gas pressure, quick-acting valves stop the feed and open a bottom drain. The compressed gas rapidly expands, forcing a rush of filtrate back across the filter medium and dislodging the cake, which drains out the bottom with the flush liquid. Of course, this technique may be used only when wet-cake discharge is permitted.

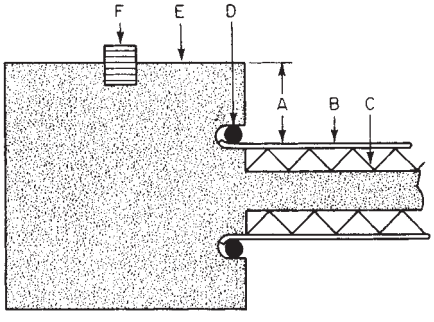


FIG. 18-114 Section detail of a caulked-gasketed-recessed filter plate: (*a*) cake recess; (*b*) filter cloth; (*c*) drainage surface of plate; (*d*) caulking strip; (*e*) plate joint; (*f*) sealing gasket. (*EIMCO Process Equipment Co.*)

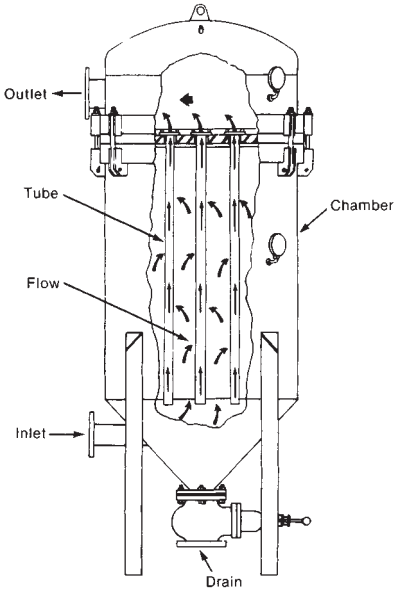


FIG. 18-115 Top-outlet tubular filter. (*Industrial Filter & Pump Mfg. Co.*)

Dry cake discharge can be achieved with a Fundabac candle-type filter manufactured by DrM, Dr. Müller, AG, of Switzerland. This filter uses a candle made up of six small-diameter tubes around a central filtrate delivery tube. This design allows the filter cloth to be flexed outward upon blowback, easily achieving an effective dry cake discharge (Fig. 18-116).

Pressure Leaf Filters Sometimes called tank filters, they consist of flat filtering elements (leaves) supported in a pressure shell. The leaves are circular, arc-sided, or rectangular, and they have filtering surfaces on both faces. The shell is a cylindrical or conical tank. Its axis may be horizontal or vertical, and the filter type is described by its shell axis orientation.

A filter leaf consists of a heavy screen or grooved plate over which a filter medium of woven fabric or fine wire cloth may be fitted. Textile fabrics are more commonly used for chemical service and are usually applied as bags that may be sewed, zippered, stapled, or snapped. Wire-screen cloth is frequently used for filter-aid filtrations, particularly if a precoat is applied. It may be attached by welding, riveting, bolting, or caulking or by the clamped engagement of two 180° bends in the wire cloth under tension, as in Multi Metal's Rim-Lok leaf. Leaves may also be of all-plastic construction. The filter medium, regardless of material, should be as taut as possible to minimize sagging when it is loaded with a cake; excessive sag can cause cake cracking or dropping. Leaves may be supported at top, bottom, or center and may discharge filtrate from any of these locations. Figure 18-117 shows the elevation section of a precoated bottom-support wire leaf.

Pressure leaf filters are operated batchwise. The shell is locked, and the prefilt slurry is admitted from a pressure source. The slurry enters in such a way as to minimize settling of the suspended solids. The shell is filled, and filtration occurs on the leaf surfaces, the filtrate discharging through an individual delivery line or into an internal manifold, as the filter design dictates. Filtration is allowed to proceed only until a cake of the desired thickness has formed, since to overfill will cause cake consolidation with consequent difficulty in washing and discharge. The decision of when to end the filtering cycle is largely a matter of experience, guided roughly by the rate in a constant-pressure filter or pressure drop in a constant-rate filter. This judgment may be supplanted by the use of a detector which "feels" the thickness of cake on a representative leaf.

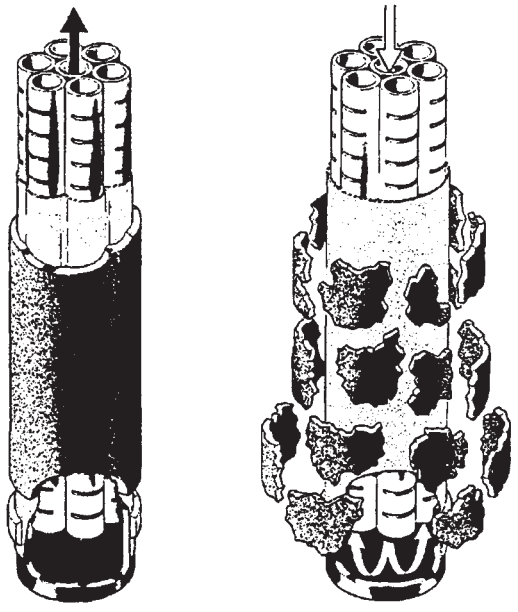


FIG. 18-116 Cake formation and discharge with the Fundabac filter element. (*DrM, Dr. Müller AG, Switzerland.*)

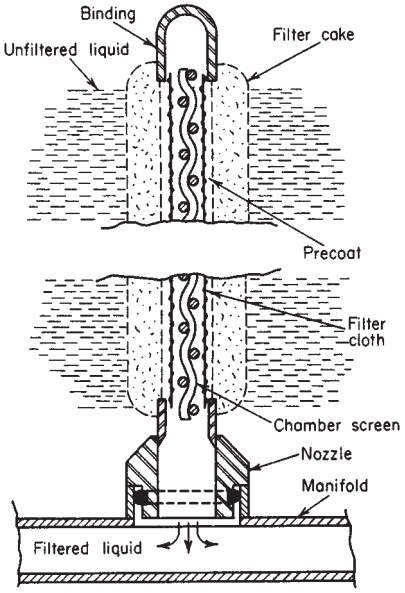


FIG. 18-117 Section of precoated wire filter leaf. (*Multi Metal Wire Cloth.*)

If the cake is to be washed, the slurry heel can be blown from the filter and wash liquor can be introduced to refill the shell. If the cake tends to crack during air blowing, it may be necessary to displace the slurry heel with wash gradually so as never to allow the cake to dry. Upon the completion of filtration and washing, the cake is discharged by one of several methods, depending on the shell and leaf configuration.

Horizontal pressure leaf filters. In these filters the leaves may be rectangular leaves which run parallel to the axis and are of varying sizes since they form chords of the shell; or they may be circular or square elements parallel to the head of the shell, and all of the same dimension. The leaves may be supported in the shell from an independent rack, individually from the shell, or from a filtrate manifold. Horizontal filters are particularly suited to dry-cake discharge.

Most of the currently available commercial horizontal pressure filters have leaves parallel to the shell head. Cake discharge may be wet or dry; it can be accomplished by sluicing with liquid sprays, vibration of the leaves, or leaf rotation against a knife, wire, or brush. If a wet-cake discharge is allowable, the filters will probably be sluiced with high-pressure liquid. If the filter has a top or bottom filtrate manifold, the leaves are usually in a fixed position, and the spray header is rotated to contact all filter surfaces. If the filtrate header is center-mounted, the leaves are generally rotated at about 3 r/min and the spray header is fixed. Some units may be wet-cake-discharged by mechanical vibration of the leaves with the filter filled with liquid. Dry-cake discharge normally will be accomplished by vibration if leaves are top- or bottom-manifolded and by rotation of the leaves against a cutting knife, wire, or brush if they are center-manifolded.

In many designs the filter is opened for cake discharge, and the leaf assembly is separated from the shell by moving one or the other on rails (Fig. 18-118). For processes involving toxic or flammable materials, a closed filter system can be maintained by sloping the bottom of the horizontal cylinder to the drain nozzle for wet discharge or by using a screw conveyor in the bottom of the shell for dry discharge (Fig. 18-119).

Vertical pressure leaf filters. These filters have vertical, parallel, rectangular leaves mounted in an upright cylindrical pressure tank. The leaves usually are of such different widths as to allow them to conform to the curvature of the tank and to fill it without waste space. The leaves often rest on a filtrate manifold, the connection being sealed by an O ring, so that they can be lifted individually from the top of the fil-

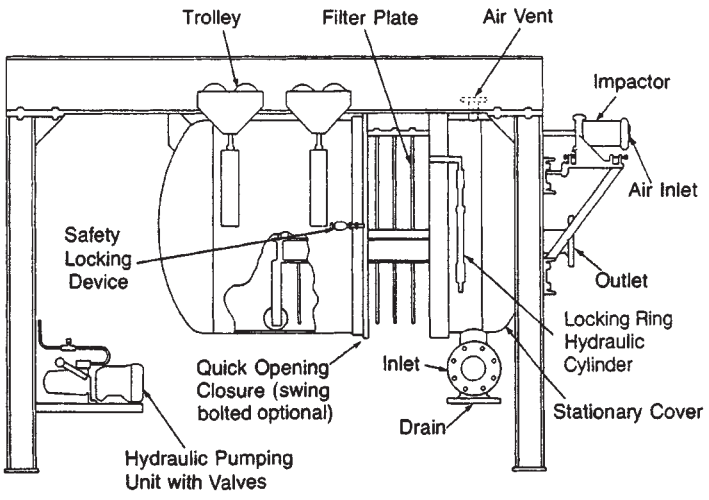


FIG. 18-118 Horizontal-tank pressure leaf filter designed for dry cake discharge. (*Sparkler Filter, Inc.*)

ter for inspection and repair. A scavenger leaf frequently is installed in the bottom of the shell to allow virtually complete filtration of the slurry heel at the end of a cycle.

Vertical filters are not convenient for the removal of dry cake, although they can be used in this service if they have a bottom that can be retracted to permit the cake to fall into a bin or hopper below. They are adapted rather to wet-solids discharge, a process that may be assisted by leaf vibration, air or steam sparging of a filter full of water, sluicing from fixed, oscillating, or traveling nozzles, and blowback. They are made by many companies, and they enjoy their widest use for filter-aid precoat filtration.

Advantages and uses. The advantages of pressure leaf filters are their considerable flexibility (up to the permissible maximum, cakes of various thickness can be formed successfully), their low labor charges, particularly when the cake may be sluiced off or the dry cake discharged cleanly by blowback, the basic simplicity of many of the designs, and their adaptability to quite effective displacement washing. Their disadvantages are the requirement of exceptionally intelligent

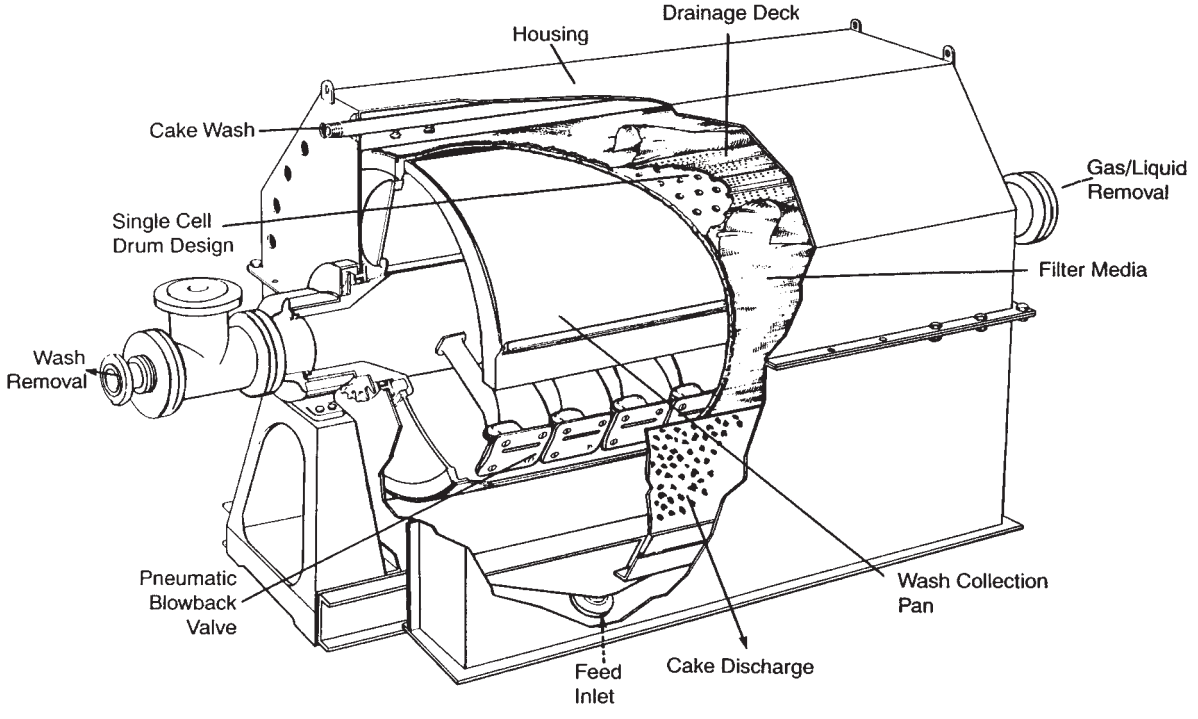


FIG. 18-119 Cutaway of a horizontal tank filter with dry-cake-discharge features. (*United States Filter.*)

and watchful supervision to avoid cake consolidation or dropping, their inability to form as dry a cake as a filter press, their tendency to classify vertically during filtration and to form misshapen nonuniform cakes unless the leaves rotate, and the restriction of most models to 610 kPa (75 psig) or less.

Pressure leaf filters are used to separate much the same kinds of slurries as are filter presses and are used much more extensively than filter presses for filter-aid filtrations. They should be seriously considered whenever uniformity of production permits long-time operation under essentially constant filtration conditions, when thorough washing with a minimum of liquor is desired, or when vapors or fumes make closed construction desirable. Under such conditions, if the filter medium does not require frequent changing, they may show a considerable advantage in cycle and labor economy over a filter press, which has a lower initial cost, and advantages of economy and flexibility over continuous vacuum filters, which have a higher first cost.

Pressure leaf filters are available with filtering areas of 930 cm^2 (1 ft^2) (laboratory size) up to about 440 m^2 (4734 ft^2) for vertical filters and 158 m^2 (1700 ft^2) for horizontal ones. Leaf spacings range from 5 to 15 cm (2 to 6 in) but are seldom less than 7.5 cm (3 in) since 1.3 to 2.5 cm (0.5 to 1 in) should be left open between surfaces.

Centrifugal-Discharge Filter Horizontal top-surface filter plates may be mounted on a hollow motor-connected shaft that serves both as a filtrate-discharge manifold and as a drive shaft to permit centrifugal removal of the cake. An example is the **Funda filter** (marketed in the United States by Steri Technologies), illustrated schematically in Fig. 18-120. The filtering surface may be a textile fabric or a wire screen, and the use of a precoat is optional. The Funda filter is driven from the top, leaving the bottom unobstructed for inlet and drainage lines; a somewhat similar machine that employs a bottom drive, providing a lower center of mass and ground-level access to the drive system, is the German-made **Schenk filter** (marketed in the United States by Schenk Filtersystems).

During filtration, the vessel that coaxially contains the assembly of filter plates is filled with prefilt under pressure, the filtrate passes through the plates and out the hollow shaft, and cake is formed on the top surfaces of the plates. After filtration, the vessel is drained, or the heel may be filtered by recirculation through a cascade ring at the top of the filter. The cake may be washed—or it may be extracted, steamed, air-blown, or dried by hot gas. It is discharged, wet or dry, by rotation of the shaft at sufficiently high speed to sling away the solids. If flushing is permitted, the discharge is assisted by a backwash of appropriate liquid.

The operating advantages of the centrifugal-discharge filter are those of a horizontal-plate filter and, further, its ability to discharge cake without being opened. It is characterized by low labor demand, easy adaptability to automatic control, and amenability to the processing of hazardous, noxious, or sterile materials. Its disadvantages are its complexity and maintenance (stuffing boxes, high-speed drive) and its cost. The Funda filter is made in sizes that cover the filtering area range of 1 to 50 m^3 (11 to 537 ft^2). The largest Schenk filter provides 100 m^2 (1075 ft^2) of area.

Continuous Cake Filters Continuous cake filters are applicable when cake formation is fairly rapid, as in situations in which slurry flow is greater than about 5 L/min (1 to 2 gal/min), slurry concentration is greater than 1 percent, and particles are greater than 0.5 μm in diameter. Liquid viscosity below 0.1 Pa·s (100 cP) is usually required for maintaining rapid liquid flow through the cake. Some designs of continuous filters can compromise some of these guidelines by sacrificial use of filter aid when the cake is not the desired product.

Rotary Drum Filters The rotary drum filter is the most widely used of the continuous filters. There are many design variations, including operation as either a pressure filter or a vacuum filter. The major difference between designs is in the technique for cake discharge, to be discussed later. All the alternatives are characterized by a horizontal-axis drum covered on the cylindrical portion by filter medium over a grid support structure to allow drainage to manifolds. Basic materials of construction may be metals or plastics. Sizes (in terms of filter areas) range from 0.37 to 186 m^2 (4 to 2000 ft^2).

All drum filters (except the single-compartment filter) utilize a rotary-valve arrangement in the drum-axis support trunnion to facilitate removal of filtrate and wash liquid and to allow introduction of air or gas for cake blowback if needed. The valve controls the relative duration of each cycle as well as providing "dead" portions of the cycle through the use of bridge blocks. A typical valve design is shown in Fig. 18-121. Internal piping manifolds connect the valve with various sections of the drum.

Most drum filters are fed by operating the drum with about 35 percent of its circumference submerged in a slurry trough, although submergence can be set for any desired amount between zero and almost total. Some units contain an oscillating rake agitator in the trough to aid solids suspension. Others use propellers, paddles, or no agitator.

Slurries of free-filtering solids that are difficult to suspend are sometimes filtered on a top-feed drum filter or filter-dryer. An example application is in the production of table salt. An alternative for slurries of extremely coarse, dense solids is the internal drum filter. In the chemical-process industry both top-feed and internal drums (which are described briefly by Emmett in Schweitzer, op. cit., p. 4-41) have largely been displaced by the horizontal vacuum filter (q.v.).

Most drum filters operate at a rotation speed in the range of 0.1 to 10 r/min. Variable-speed drives are usually provided to allow adjustment for changing cake-formation and drainage rates.

Drum filters commonly are classified according to the feeding arrangement and the cake-discharge technique. They are so treated in this subsection. The characteristics of the slurry and the filter cake usually dictate the cake-discharge method.

Scraper-Discharge Filter The filter medium is usually caulked into grooves in the drum grid, with cake removal facilitated by a scraper blade just prior to the resubmergence of the drum (Fig. 18-122). The scraper serves mainly as a deflector to direct the cake, dislodged by an

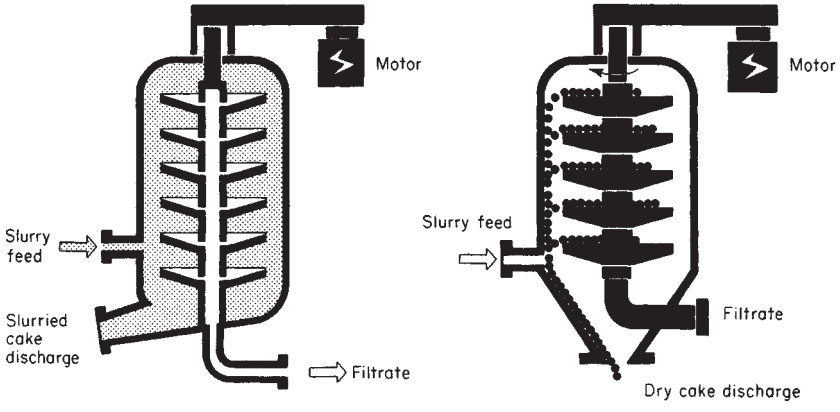


FIG. 18-120 Schematic of a centrifugal-discharge filter. (*Steri Technologies.*)

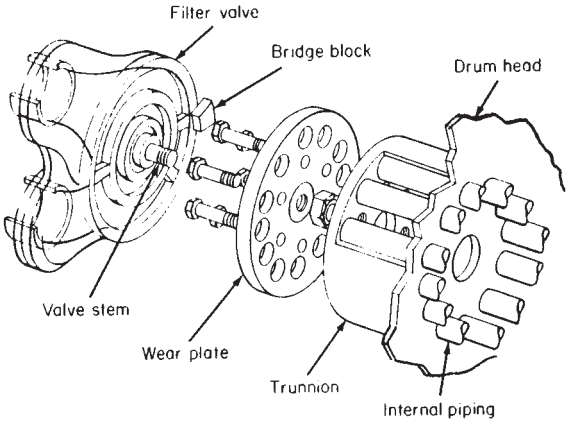


FIG. 18-121 Component arrangement of a continuous-filter valve. (*EIMCO Process Equipment Co.*)

air blowback, into the discharge chute, since actual contact with the medium would cause rapid wear. In some cases the filter medium is held by circumferentially wound wires spaced 50 mm (2 in) apart, and a flexible scraper blade may rest lightly against the wire winding. A taut wire in place of the scraper blade may be used in some applications in which physical dislodging of sticky, cohesive cakes is needed.

For a given slurry, the maximum filtration rate is determined by the minimum cake thickness which can be removed—the thinner the cake, the less the flow resistance and the higher the rate. The minimum thickness is about 6 mm (0.25 in) for relatively rigid or cohesive cakes of materials such as mineral concentrates or coarse precipitates like gypsum or calcium citrate. Solids that form friable cakes composed of less cohesive materials such as salts or coal will usually require a cake thickness of 13 mm (0.5 in) or more. Filter cakes composed of fine precipitates such as pigments and magnesium hydroxide, which often produce cakes that crack or adhere to the medium, usually need a thickness of at least 10 mm (0.38 in).

String-Discharge Filter A system of endless strings or wires spaced about 13 mm (0.5 in) apart pass around the filter drum but are separated tangentially from the drum at the point of cake discharge, lifting the cake off as they leave contact with the drum. The strings return to the drum surface guided by two rollers, the cake separating from the strings as they pass over the rollers. If it has the required body, a thinner cake (5 mm or about 3/16 in) than can be handled by drum filters is feasible, allowing more difficult materials to be filtered. This is done at the expense of greater dead area on the drum. Success depends on the ability of the cake to be removed with the strings and must be determined experimentally. Applications are mainly in the starch and pharmaceutical industries, with some in the metallurgical field.

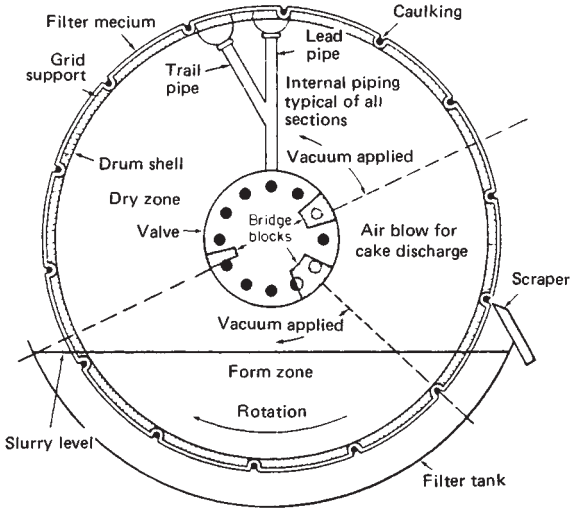


FIG. 18-122 Schematic of a rotary-drum vacuum filter with scraper discharge, showing operating zones. (*Schweitzer,* Handbook of Separation Techniques for Chemical Engineers, *p. 4-38. Copyright 1979 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Inc.*)

Removable-Medium Filters Some drum filters provide for the filter medium to be removed and reapplied as the drum rotates. This feature permits the complete discharge of thin or sticky cake and provides the regenerative washing of the medium to reduce blinding. Higher filtration rates are possible because of the thinner cake and clean medium, but this is compromised by a less pure filtrate than normally produced by a nonremovable medium.

Belt-discharge filter. This is a drum filter carrying a fabric that is removed, passed over rollers, washed, and returned to the drum. Figure 18-123 shows the path of the medium while it is off the drum. A special aligning device keeps the medium wrinkle-free and in proper line during its travel. Thin cakes of difficult solids which may be slightly soluble are good applications. When acceptable, a sluice discharge makes cakes as thin as 1.5 to 2 mm (about 1/16 in) feasible. Several manufacturers offer belt-discharge filters.

Coilfilter. The **Coilfilter** (Komline-Sanderson Engineering Corp.) is a drum filter with a medium consisting of one or two layers of stainless-steel helically coiled springs, about 10 mm (0.4 in) in diameter, placed in a corduroy pattern around the drum. The springs follow the drum during filtration with cake forming the coils. They are separated from the drum to discharge the cake and undergo washing; if two layers are used, the coils of each layer are further separated from those of the other, passing over different sets of rolls. The use of stainless steel in spring form provides a relatively permanent medium that is readily cleaned by washing and flexing. Filtrate clarity is poorer than with most other media, and a relatively large vacuum pump is needed to handle greater air leakage than is characteristic of fabric media. Material forming a slimy, matlike cake (e.g., raw sewage) is the typical application.

Roll-Discharge Filters A roll in close proximity to the drum at the point of cake discharge rotates in the opposite direction at a peripheral speed equal to or slightly faster than that of the drum (Fig. 18-124). If the cake on the drum is adequately tacky and cohesive for this discharge technique, it adheres to cake on the smaller roll and separates from the drum. A blade or taut wire removes the material from the discharge roll. This design is especially good for thin, sticky cakes. If necessary, a slight air blow may be provided to help release the cake from the drum. Typical cake thickness is 1 to 10 mm (0.04 to 0.4 in).

Single-Compartment Drum Filter

Bird-Young filter. This filter (Bird Machine Co.) differs from most drum filters in that the drum is not compartmented and there is no internal piping or rotary valve. The entire inside of the drum is sub-

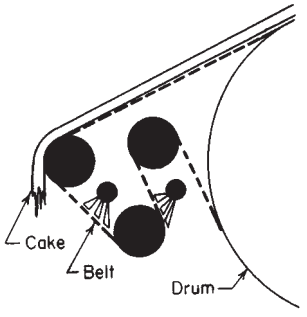


FIG. 18-123 Cake discharge and medium washing on an EIMCO belt filter. (*EIMCO Process Equipment Co.*)

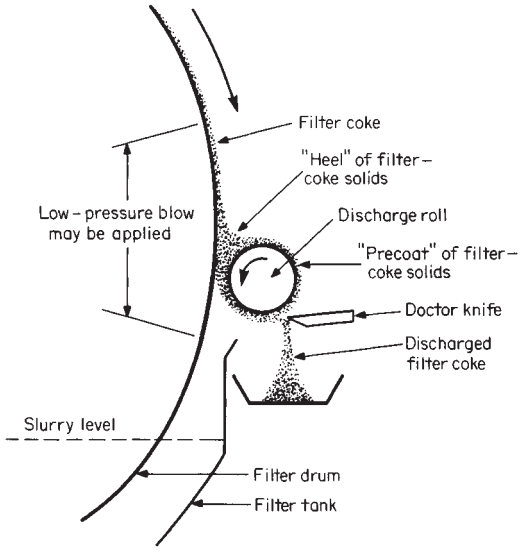


FIG. 18-124 Operating principles of a roll-discharge mechanism. (*Schweitzer,* Handbook of Separation Techniques for Chemical Engineers, *p. 4-40. Copyright 1979 by McGraw-Hill, Inc. Used with permission of McGraw-Hill Book Co.*)

jected to vacuum, with its surface perforated to pass the filtrate. Cake is discharged by an air blowback applied through a "shoe" that covers a narrow discharge zone on the inside surface of the drum to interrupt the vacuum, as illustrated in Fig. 18-125. The internal drum surface must be machined to provide close clearance of the shoe to avoid leakage. The filter is designed for high filtration rates with thin cakes. Rotation speeds to 40 r/min are possible with cakes typically 3 to 6 mm (0.12 to 0.24 in) thick. Filter sizes range from 930 cm^2 to 19 m^2 (1 to 207 ft^2) with 93 percent of the area active. The slurry is fed into a conical feed tank designed to prevent solids from settling without the use of mechanical agitators. The proper liquid level is maintained by overflow, and submergence ranges from 5 to 70 percent of the drum circumference.

The perforated drum cylinder is divided into sections about 50 to 60 mm (2 to 2.5 in) wide. The filter medium is positioned into tubes between the sections and locked into place by round rods. No caulking, wires, or other fasteners are needed.

Wash sprays may be applied to the cake, with collection troughs or pans inserted inside the drum to keep the wash separate from the filtrate. Filtrate is removed from the lower section of the drum by a pipe passing through the trunnions.

The major advantages of the Bird-Young filter are its ability to handle thin cakes and operate at high speeds, its washing effectiveness, and its low internal resistance to air and filtrate flow. An additional advantage is the possibility of construction as a pressure filter with up to 1.14-MPa (150-psig) operating pressure to handle volatile liquids. The chief disadvantages are its high cost and the limited flexibility imposed by not having an adjustable rotary valve. Best applications are on free-draining nonblinding materials such as paper pulp or crystallized salts.

Continuous Pressure Filters These filters consist of conventional drum or disk filters totally enclosed in pressure vessels. Filtration takes place with the vessel pressurized up to 6 bar and the filtrate discharging either at atmospheric pressure or into a receiver maintained at a suitable backpressure. Cake discharge is facilitated through a dual valve and lock-hopper arrangement in order to maintain vessel pressure. Alternatively, the discharged filter cake can be reslurried within the filter or in an adjoining pressure vessel and removed through a control valve.

One variation in design, the Ceramec, offered by Outokumpu Mintec, employs "gasless" ceramic media instead of traditional filter fabrics, relying partly on capillary action to achieve low moistures.

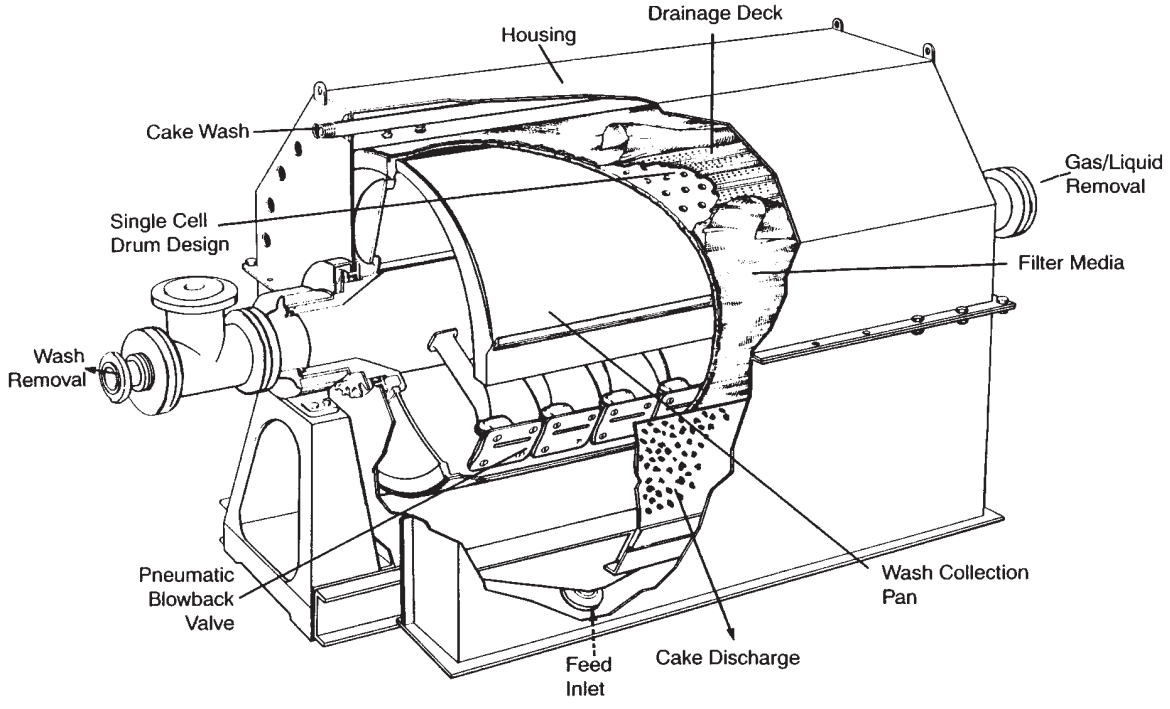


FIG. 18-125 Cutaway of the single-compartment drum filter. (*Bird Machine Co.*)

This results in a significant drop in power consumption by greatly reducing the compressed air requirements.

Continuous Precoat Filters These filters may be operated as either pressure or vacuum filters, although vacuum operation is the prevailing one. The filters are really not continuous but have an extremely long batch cycle (1 to 10 days). Applications are for continuous clarification of liquids from slurries containing 50 to 5000 ppm of solids when only very thin unacceptable cakes would form on other filters and where "perfect" clarity is required.

Construction is similar to that of other drum filters, except that vacuum is applied to the entire rotation. Before feeding slurry a precoat layer of filter aid or other suitable solids, 75 to 125 mm (3 to 5 in) thick, is applied. The feed slurry is introduced and trapped in the outer surface of the precoat, where it is removed by a progressively advancing doctor knife which trims a thin layer of solids plus precoat (Fig. 18-126). The blade advances 0.05 to 0.2 mm (0.002 to 0.008 in) per revolution of the drum. When the precoat has been cut to a predefined minimum thickness, the filter is taken out of service, washed, and freshly precoated. This turnaround time may be 1 to 3 h.

Disk Filters A disk filter is a vacuum filter consisting of a number of vertical disks attached at intervals on a continuously rotating horizontal hollow central shaft (Fig. 18-127). Rotation is by a gear drive. Each disk consists of 10 to 30 sectors of metal, plastic, or wood, ribbed on both sides to support a filter cloth and provide drainage via an outlet nipple into the central shaft. Each sector may be replaced individually. The filter medium is usually a cloth bag slipped over the sectors and sealed to the discharge nipple. For some heavy-duty applications on ores, stainless-steel screens may be used.

The disks are typically 30 to 50 percent submerged in a troughlike vessel containing the slurry. Another horizontal shaft running beneath the disks may contain agitator paddles to maintain suspension of the solids, as in the EIMCO **Agidisc filter.** In some designs, feed is distributed through nozzles below each disk. Vacuum is supplied to the sectors as they rotate into the liquid to allow cake formation. Vacuum is maintained as the sectors emerge from the liquid and are exposed to air. Wash may be applied with sprays, but most applications are for dewatering only. As the sectors rotate to the discharge point, the vacuum is cut off, and a slight air blast is used to loosen the cake. This allows scraper blades to direct the cake into discharge chutes positioned between the disks. Vacuum and air blowback is controlled by an automatic valve as in rotary-drum filters.

Of all continuous filters, the vacuum disk is the lowest in cost per unit area of filter when mild steel, cast iron, or similar materials of construction may be used. It provides a large filtering area with minimum floor space, and it is used mostly in high-tonnage dewatering applications in sizes up to about 300 m^2 (3300 ft^2) of filter area.

The main disadvantages are the inadaptability to have effective wash and the difficulty of totally enclosing the filter for hazardous-material operations.

Horizontal Vacuum Filters These filters are generally classified into two broad classes: rotary circular and belt-type units. Regardless of geometry, they have similar advantages and limitations. They provide flexibility of choice of cake thickness, washing time, and drying cycle. They effectively handle heavy, dense solids, allow flooding of the cake with wash liquor, and are easily designed for true countercurrent leaching or washing. The disadvantages are they are more expensive to build than drum or disk filters, they use a large amount of floor space per filter area, and they are difficult to enclose for hazardous applications.

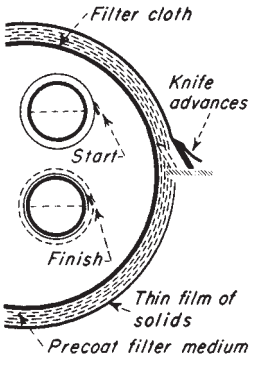


FIG. 18-126 Operating method of a vacuum precoat filter. (*Dorr-Oliver, Inc.*)

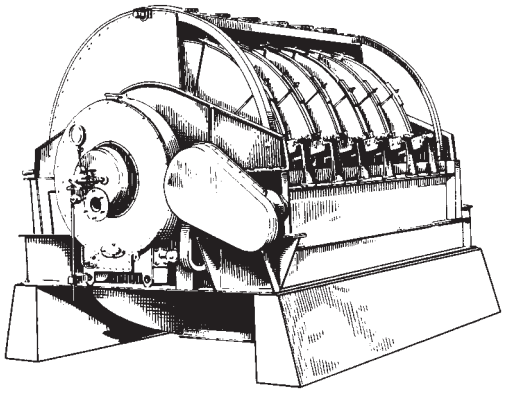


FIG. 18-127 Rotary disk filter. (*Dorr-Oliver, Inc.*)

Horizontal-Table, Scroll-Discharge, and Pan Filters These are all basically revolving annular tables with the top surface a filter medium (Fig. 18-128). The table is divided into sectors, each of which is a separate compartment. Vacuum is applied through a drainage chamber beneath the table that leads to a large rotary valve. Slurry is fed at one point, and cake is removed after completing more than three-fourths of the circle, by a horizontal scroll conveyor which elevates the cake over the rim of the filter. A clearance of about 10 mm (0.4 in) is maintained between the scroll and the filter medium to prevent damage to the medium. Residual cake on the medium may be loosened by an air blow from below or with high-velocity liquid sprays from above. This residual cake is a disadvantage peculiar to this type of filter. With material that can cause blinding, frequent shutdowns for thorough cleaning may be needed. Unit sizes range from about 0.9 to 7 m (3 to 24 ft) in diameter, with about 80 percent of the surface available for filtration.

Tilting-Pan Filter This is a modification of the table or pan filter in which each of the sectors is an individual pan pivoted on a radial axis to allow its inversion for cake discharge, usually assisted by an air blast. Filter-cake thicknesses of 50 to 100 mm (2 to 4 in) are common. Most applications involve free-draining inorganic-salt dewatering. In addition to the advantages and disadvantages common to all horizontal continuous filters, tilting-pan filters have the relative advantages of complete wash containment per sector, good cake discharge, filter-medium washing, and feasibility of construction in very large sizes, up to about 25 m (80 ft) in diameter, with about 75 percent of the area usable. Relative disadvantages are high capital cost (especially in smaller sizes) and mechanical complexity leading to higher maintenance costs.

Horizontal-Belt Filter This filter consists of a slotted or perforated elastomer drainage belt driven as a conveyor belt carrying a filter fabric belt (Fig. 18-129). Both belts are supported by and pass across a lubricated support deck. A vacuum pan, aligned with the slots in the elastomer belt, forms a continuous vacuum surface which may include multiple zones for cake formation, washing and final dewatering. Several manufacturers provide horizontal-belt filters, the major differences among which lie in the construction of the drainage belt, the method of retaining the slurry/cake on the belt, and the method of maintaining the alignment of the filter medium. The filters are rated according to the available active filtration area. *Indexing horizontal-belt filters* do away with the elastomer drainage belt of the original design in favor of large drainage pans directly beneath the filter medium. Either the pans or the filter medium is indexed to provide a

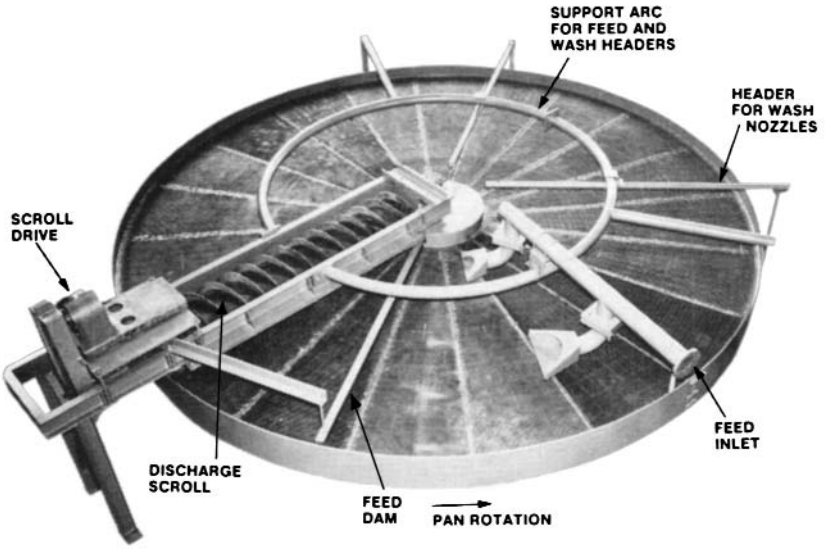


FIG. 18-128 Continuous horizontal vacuum table filter. (*Dorr-Oliver, Inc.*)

pseudo-continuous filtration operation. The applied vacuum is cycled with the indexing operation to minimize wear to the sliding surfaces. As a result the indexing filter must be de-rated for the indexing cycle. The indexing horizontal-belt filter avoids the problem of process compatibility with the elastomer drainage belt. The major differences among the indexing machines of several manufacturers lie in the method of indexing and the method of cycling the applied vacuum.

The method of feeding, washing, dewatering and discharging is essentially the same with all horizontal-belt filters. Slurry is fed at one end by overflow weirs or a fantail chute; wash liquor, if required, is applied by sprays or weirs at one or more locations as the formed cake moves along the filter. Wiping dams and separations in the drainage pan(s) provide controlled wash application. The cake is discharged as the filter-medium belt passes over the end pulley after separation from the drainage surface. Separating the filter-medium from the drainage surface allows thorough spray cleaning of the filter-medium belt. The duration of the filtration cycle is controlled by belt speed which may be as high as 1 m/s (3.3 ft/s) and is typically variable. The minimum possible cake thickness, at a given solids loading, which can be effectively discharged limits the belt speed from a process point of view. The maximum cake thickness is dependent on the method used to retain the slurry during cake formation and can be 100 to 150 mm (4 to 6 in) with fast draining materials.

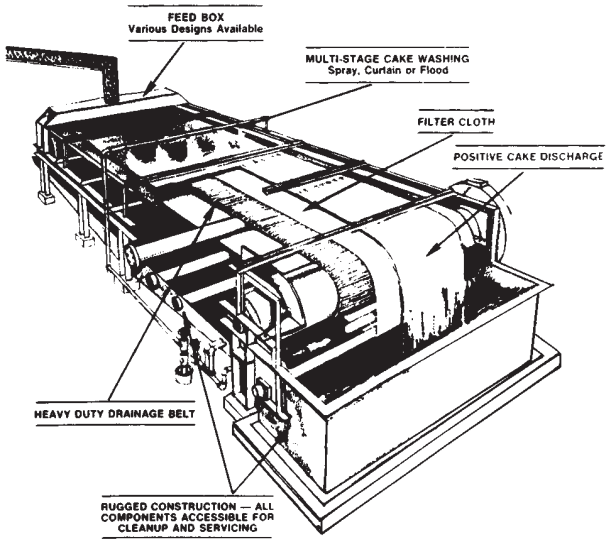


FIG. 18-129 Horizontal-belt filter. (*EIMCO Process Equipment Co.*)

Some of the advantages of horizontal-belt filters are the precise control of the filtration cycle including the capability for countercurrent washing of the cake, effective cake discharge and thorough cleaning of the filter medium belt. The horizontal-belt filter's primary disadvantage is that at least half of the filtration medium is always idle during the return loop. This contributes to a significantly higher capital cost which can be two to four times that of a drum or disk filter with equal area. Horizontal-belt filters with active filtration area ranging from 0.18 m^2 to 120 m^2 (2 ft^2 to 1300 ft^2) on a single machine have been installed.

Additional equipment is sometimes integrated with horizontal-belt filters to further dewater the cake through expression. The addition of such equipment shouldn't be confused with expression equipment that utilizes filter medium belts. Belt type expression equipment is described later in the "Expression" subsection.

Filter Thickeners Thickeners are devices which remove a portion of the liquid from a slurry to increase the concentration of solids in suspension. Thickening is done to prepare a dilute slurry for more economical filtration or to change the consistency or concentration of the slurry for process reasons. The commonest method of thickening is by gravity sedimentation, discussed earlier in this section. Occasions may arise, however, in which a filter may be called upon for thickening service. Many of the filters previously discussed as cake filters can be operated as thickeners: the filter press with special plates containing flow channels that keep velocity high enough to prevent cake buildup, cycled tube or candle filters with the cake discharge into the filter tank, and continuous leaf filters which use rotating elements adjacent to the filtering surfaces to limit filter cake buildup. Examples of these filters include the Shriver Thickener, the Industrial Hydra-Shoc Filter employing Back Pulse Technology, the DrM, Dr. Müller AG, Contibac Thickener, and the Ingersoll Rand Continuous Pressure Filter.

Clarifying Filters Clarifying filters are used to separate liquid mixtures which contain only very small quantities of solids. When the

solids are finely divided enough to be observed only as a haze, the filter which removes them is sometimes called a polishing filter. The prefilt slurry generally contains no more than 0.10 percent solids, the size of which may vary widely (0.01 to 100 μm). The filter usually produces no visible cake, sometimes because the amount of solids removed is so small, sometimes because the particles are removed by being entrapped within rather than upon the filter medium. Compared with cake filters, clarifying filters are of minor importance to pure chemical-process work, their greatest use being in the fields of beverage and water polishing, pharmaceutical filtration, fuel- and lubricating-oil clarification, electroplating-solution conditioning, and dry-cleaning-solvent recovery. They are essential, however, to the processes of fiber spinning and film extrusion; the spinning solution or dope must be free of particles above a certain size to maintain product quality and to prevent the clogging of spinnerets.

Most cake filters can be so operated as to function as clarifiers, although not necessarily with efficiency. On the other hand, a number of clarifying filters which can be used for no purpose other than clarifying or straining have been developed. In general, clarifying filters are less expensive than cake filters. Clarifying filters may be classified as disk and plate presses, cartridge clarifiers, precoat pressure filters, deep-bed filters, and miscellaneous types. Membrane filters constitute a special class of plate presses and cartridge filters. Simple strainers sometimes are used as clarifiers of liquids containing very large particles. Because they more closely resemble wet screens than filters and because they have little primary process application, they are not discussed here.

Disk Filters and Plate Presses Filters employing asbestos-pulp disks, cakes of cotton fibers (filtermasse), or sheets of paper or other media are used widely for the polishing of beverages, plating solutions, and other low-viscosity liquids containing small quantities of suspended matter. The term **disk filter** is applied to assemblies of pulp disks made of asbestos and cellulose fibers and sealed into a pressure case. The disks may be preassembled into a self-supporting unit (Fig. 18-130), or each disk may rest on an individual screen or plate against which it is sealed as the filter is closed (Fig. 18-131). The liquid flows through the disks, and into a central or peripheral discharge manifold. Flow rates are on the order of 122 L/(min·m^2) [3 gal/(min·ft^2)], and the operating pressure does not normally exceed 345 kPa (50 psig) (usually it is less). Disk filters are almost always operated as pressure filters. Individual units deliver up to 378 L/min (6000 gal/h) of low-viscosity liquid.

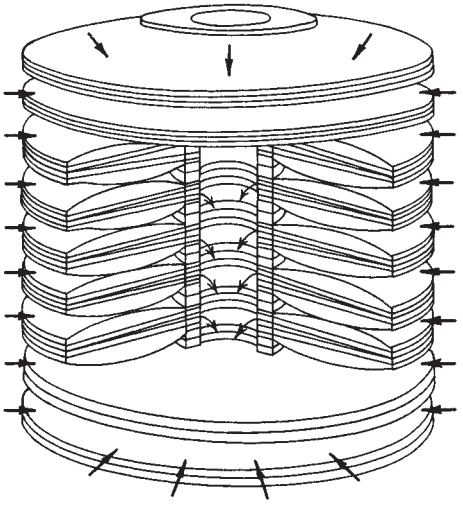


FIG. 18-130 Preassembled pack of clarifying-filter disks. (*Alsop Engineering Co.*)

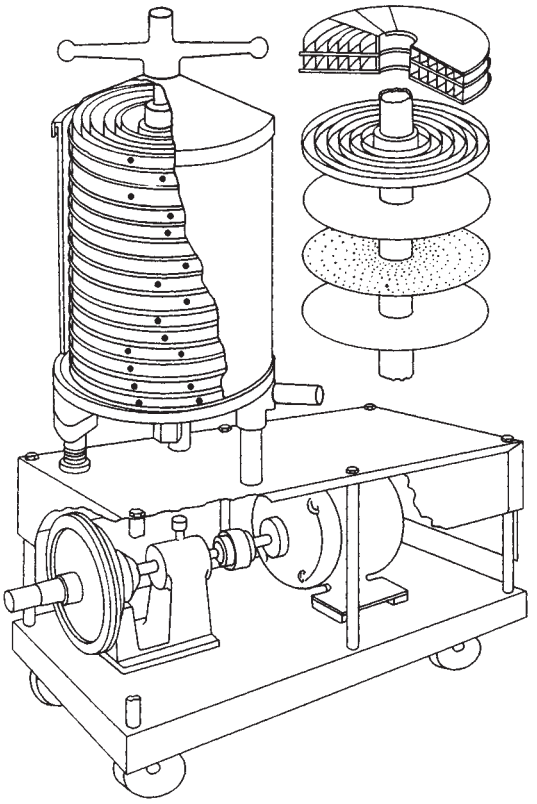


FIG. 18-131 Disk-and-plate clarifying-filter assembly. (*Alsop Engineering Co.*)

Disk-and-plate assemblies somewhat resemble horizontal-plate pressure filters, which, in fact, may be used for polishing. In one design (**Sparkler VR filter**) both sides of each plate are used as filtering surfaces, having paper or other media clamped against them.

Pulp filters. These filters employ one or more packs of filtermasse (cellulose fibers compressed to a compact cylinder) stacked into a pressure case. The packs are sometimes supported in individual trays which provide drainage channels and sometimes rest on one another with a loose spacer plate between each two packs and with a drainage screen buried in the center of each pack. The liquid being clarified flows under a pressure of 345 kPa (50 psig) or less through the pulp packs and into a drainage manifold. Flow rates are somewhat less than for disk filters, on the order of 20 L/(min·m^2) [0.5 gal/(min·ft^2)]. Pulp filters are used chiefly to polish beverages. The filtermasse may be washed in special washers and re-formed into new cakes.

Plate presses. Sometimes called sheet filters, these are assemblies of plates, sheets of filter media, and sometimes screens or frames. They are essentially modified filter presses with practically no cake-holding capacity. A press may consist of many plates or of a single filter sheet between two plates, the plates may be rectangular or circular, and the sheets may lie in a horizontal or vertical plane. The operation is similar to that of a filter press, and the flow rates are about the same as for disk filters. The operating pressure usually does not exceed 138 kPa (20 psig). The presses are used most frequently for low-viscosity liquids, but an ordinary filter press with thin frames is commonly used as a clarifier for 100-Pa·s (1000-P) rayon-spinning solution. Here the filtration pressure may be 6900 kPa (1000 psig).

Disk, pulp, and sheet filters accomplish extreme clarification. Not infrequently their mission is complete removal of particles above a

stipulated cut size, which may be much less than 1 μm. They operate over a particle-size range of four to five orders of magnitude, contrasting with two orders of magnitude for most other filters. It is not surprising, therefore, that they involve a variety of kinds and grades of filter media, often in successive stages. In addition to packs or disks of cellulosic, polymeric, or asbestos fiber, sheets of pulp, paper, asbestos, carded fiber, woven fabrics, and porous cellophane or polymer are employed. Sandwich-pack composites of several materials have been used for viscous-dope filtration.

The use of asbestos has been greatly diminished because of its identification with health hazards. There have been proposed replacement materials such as the **Zeta Plus** filter media from the AMF Cuno Division, consisting of a composite of cellulose and inorganic filter aids that have a positive charge and provide an electrokinetic attraction to hold colloids (usually negatively charged). These media therefore provide both mechanical straining and electrokinetic adsorption.

Cartridge Clarifiers Cartridge clarifiers are units which consist of or use one or more replaceable or renewable cartridges containing the active filter element. The unit usually is placed in a line carrying the liquid to be clarified; clarification thus occurs while the liquid is in transit.

Mechanical or edge filters. These consist of stacks of disks separated to precise intervals by spacer plates, or a wire wound on a cage in grooves of a precise pitch, or a combination of the two. The liquid to be filtered flows radially between the disks, wires, or layers of paper, and particles larger than the spacing are screened out. Edge filters can remove particles down to 0.001 in (25 μm) but more often have a minimum spacing of twice this value. They have small solids-retaining capacity and hence must be cleaned often to avoid plugging. Continuous cleaning is provided in some filters. For example, the Cuno **Flo-Klean** (Fig. 18-132), a wire-wound unit, employs a slowly rotating nozzle which backwashes the element with filtered liquid; and the Cuno **Auto-Klean** is equipped with a scraper that fits into the interdisk slots to comb away accumulated solids. In either case, the dislodged solids fall into a sump that may be drained at intervals.

Micronic clarifiers. The greatest number of cartridge clarifiers are of the micronic class, with elements of fiber, resin-impregnated filter paper, porous stone, or porous stainless steel of controlled porosity. Other rustless metals are also available. The elements may be chosen to remove particles larger than a fraction of a micrometer, although many are made to pass 10-μm solids and smaller. By proper choice of multiple-cylinder cartridges or multiple cartridges in parallel any desired flow rate can be obtained at a reasonable pressure drop, often less than 138 kPa (20 psig).

When the pressure rises to the permissible maximum, the cartridge must be opened and the element replaced. Micronic elements of the fiber type cannot be cleaned and are so priced that they can be discarded or the filter medium replaced economically. Stone elements usually must be cleaned, a process best accomplished by the manufacturer of the porous ceramic or in accordance with the manufacturer's directions. The user can clean stainless-steel elements by chemical treatment.

Flexibility. Cartridge filters are flexible: cartridges of different ratings and materials of construction can be interchanged, permitting ready accommodation to shifting conditions. They have the disadvantage of very limited solid-handling capability so that the maximum solid concentrations in the feed are limited to about 0.01 percent solids. The biggest limitation for modern process-plant operation is the need to open the filter to replace cartridges, which makes their use for the processing of hazardous materials undesirable. Some manufacturers—for example, the Hydraulic Research Division of Textron Inc. and the Fluid Dynamics Division of Brunswick Corp.—have designed cartridges of bonded metal fibers that can be back-flushed or chemically cleaned without opening the unit. These filters, which can operate at temperatures to 482°C (900°F) and at pressures of 33 MPa (325 atm) or greater, are particularly useful for filtering polymers.

Granular Media Filters Many types of granular media filters are used for clarification, operating either as gravity or pressure filters. Gravity filters rely on a difference in elevation between inlet and outlet to provide the driving force necessary to force the liquid through the granular media. Pressure filters employ enclosed vessels operating at relatively low pressure differentials, in the order of 50 to 70 kPa (7 to 10 psig), which may function in either an upflow or a downflow mode.

The media may be a single material, such as sand, but more often will consist of two or even three layers of different materials, such as anthracite coal in the top layer and sand in the lower one. Solids are captured throughout the bed depth, rather than on the surface, and the gradient in void size provides substantially more solids-holding capacity. The anthracite layer, typically employing 1-mm grain size, serves as a roughing filter and also provides a flocculating action which helps the finer sand, ~0.5-mm particle size, to serve as an effective polishing zone. Media depths vary, but 0.7 to 1.0 m is typical of a dual media installation. Deeper beds of up to 2.5 m (8 ft) are employed in some cases involving special applications where greater solids-holding capacity is desired.

Filtrate is collected in the underdrain system, which may be as simple as a network of perforated pipes covered by graded gravel or a complex structure with slotted nozzles or conduits that will retain the finest sand media while maintaining high flow rates. This latter design allows the use of both air and liquid for the backwashing and cleaning operations.

Backwashing usually is carried out when a limiting pressure drop is reached and before the bed becomes nearly filled with solids, which would lead to a deterioration in filtrate clarity. Cleaning the media is greatly aided by the use of an air scour which helps break loose the trapped solids and provides efficient removal of this material in the subsequent backflushing step. The filtration action tends to agglomerate the filtered solids and, as a result, these generally will settle out readily from the backwash fluid. If the filter is handling a clarifier overflow, usually it is possible to discharge the backwash liquid into the clarifier without risk of these solids returning to the filter. Filter media consumption is low, with normal replacement usually being less than 5 percent per year.

These filters are best applied on relatively dilute suspensions, <150 mg/L suspended solids, allowing operation at relatively high rates, 7.5

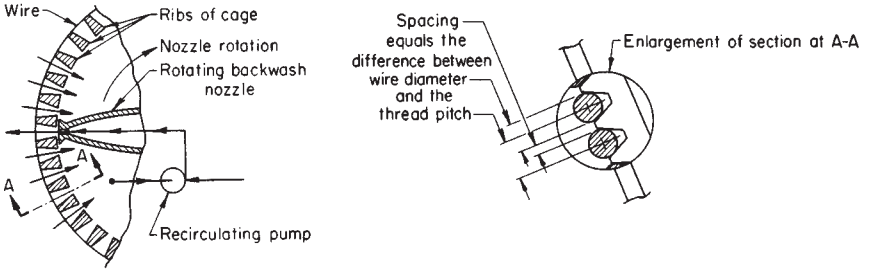


FIG. 18-132 Sectional view of the Cuno Flo-Klean backwashing edge filter. Fluid pumped through the nozzle loosens solids from the filter surface and clears the filtering area. The pump draws filtered fluid from the filter discharge and returns it to the system through the nozzle. Thus, there is no loss of backwash fluid. (*Cuno Division, AMF, Inc.*)

to 15.0 $m^3/m^2/h$ (3 to 6 gpm/ft^2). Solids capture will range from 90 to 98 percent in a well-designed system. Typical operating cycles range from 8 to 24 h of filtration (and up to 48 h in municipal water treatment), followed by a backwash interval of 15 to 30 min. Applications are principally in municipal and wastewater treatment, but granular media filters also have been employed in industrial uses such as pulp and paper plant inlet water treatment; removal of oil, grease, and scale from steelmaking process wastewater; and clarification of electrolyte in copper electrowinning operations.

United States Filter Corp. Maxi-Flo Filter. The **Maxi-Flo Filter** is an example of the upflow closed-vessel design. Filtration rates to 0.0081 $m^3/(m^2 \cdot s)$ [12 gal/(ft^2·min)] and filter cross-section areas up to 10.5 m^2 (113 ft^2) are possible. Deep-bed filtration has been reviewed by Tien and Payatakes [*Am. Inst. Chem. Eng. J.*, **25,** 737 (1970)] and by Oulman and Baumann [*Am. Inst. Chem. Eng. Symp. Ser.*, **73**(171), 76 (1977)].

Dyna Sand Filter. A filter that avoids batch backwashing for cleaning, the **Dyna Sand Filter** is available from Parkson Corporation. The bed is continuously cleaned and regenerated by recycling solids internally through an air-lift pipe and a sand washer. Thus a constant pressure drop is maintained across the bed, and the need for parallel filters to allow continued on-stream operation, as with conventional designs, is avoided.

Miscellaneous Clarifiers Various types of filters such as cartridge, magnetic, and bag filters are widely used in polishing operations, generally to remove trace amounts of suspended solids

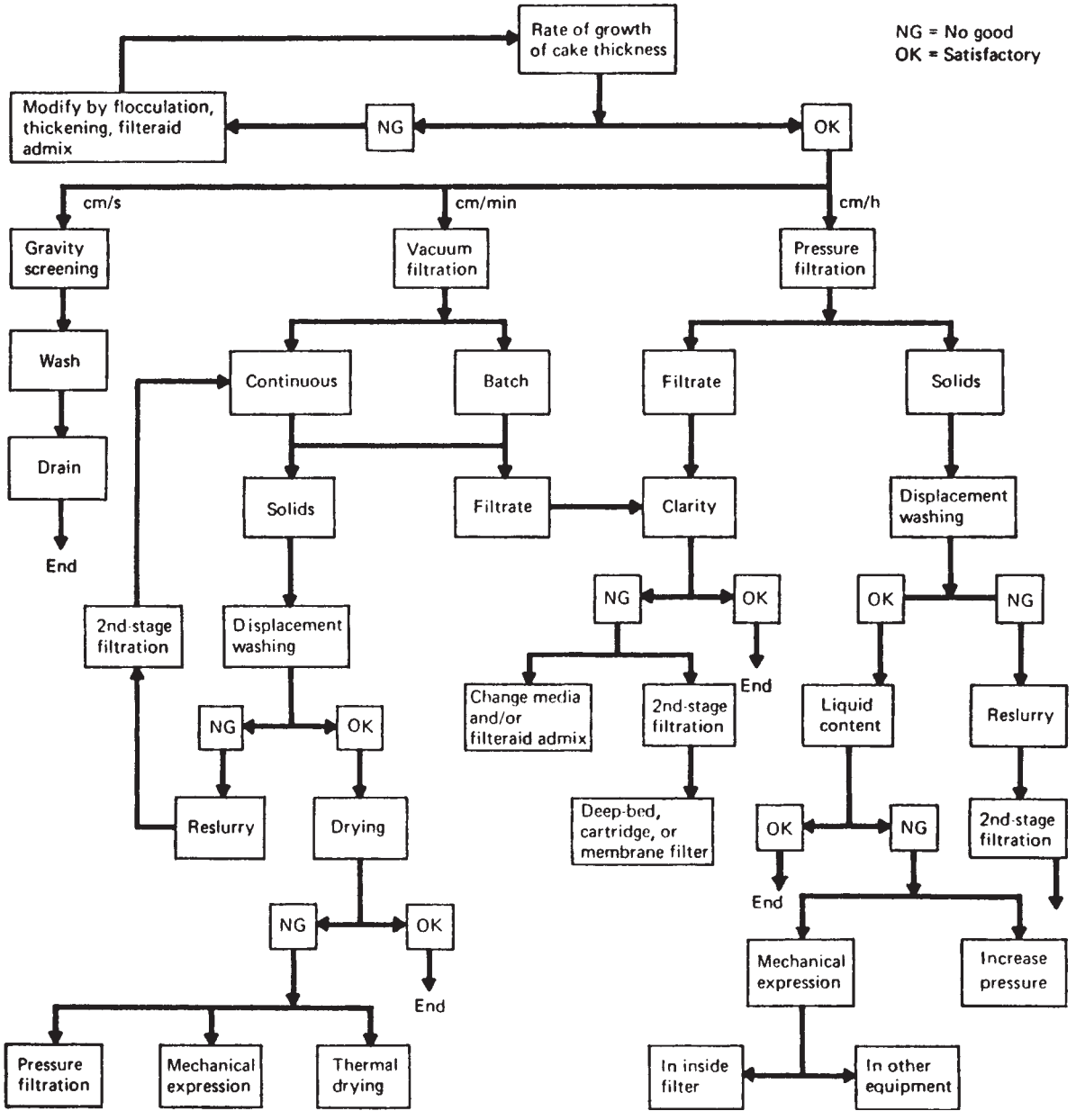


FIG. 18-133 Decision pattern for solving a filtration problem. [*Tiller,* Chem. Eng., ***81****(9), 118 (1974), by permission.*]

remaining from prior unit operations. A thorough discussion of cartridge and felt strainer bag filters is available in Schweitzer, op. cit., Section 4.6 (Nickolaus) and Section 4.7 (Wrotnowski).

SELECTION OF FILTRATION EQUIPMENT

If a process developer who must provide the mechanical separation of solids from a liquid has cleared the first decision hurdle by determining that filtration is the way to get the job done (see the final subsection of Sec. 18, "Selection of a Solids-Liquid Separator")—or that it must remain in the running until some of the details of equipment choice have been settled—choosing the right filter and right filtration conditions may still be difficult. Much as in the broader determination of which unit operation to employ, the selection of filtration equipment involves the balancing of process specifications and objectives against capabilities and characteristics of the various equipment choices (including filter media) available. The important process-related factors are slurry character, production throughput, process conditions, performance requirements, and permissible materials of construction. The important equipment-related factors are type of cycle (batch or continuous), driving force, production rates of the largest and smallest units, separation sharpness, washing capability, dependability, feasible materials of construction, and cost. The estimated cost must account for installed cost, equipment life, operating labor, maintenance, replacement filter media, and costs associated with product-yield loss (if any). In between the process and equipment factors are considerations of slurry preconditioning and use of filter aids.

Slurry characteristics determine whether a clarifying or a cake filter is appropriate; and if the latter, they determine the rate of formation and nature of the cake. They affect the choice of driving force and cycle as well as specific design of machine.

There are no absolute selection techniques available to come up with the "best" choice since there are so many factors involved, many of them difficult to make quantitative and, not uncommonly, some contradictory in their demands. However, there are some published general suggestions to guide the thinking of the engineer who faces the selection of filtration equipment. Figure 18-133 is a decision tree designed by Tiller [*Chem. Eng.*, **81**(9), 118 (1974)] to show the steps to be followed in solving a filtration problem. It is erected on the premise that rate of cake formation is the most important guide to equipment selection. A filter-selection process proposed by Purchas (op. cit., pp. 10–14) employs additional criteria and is based on a combination of process specifications and the results of simple tests. The application is coded by use of Figs. 18-134, 18-135, and 18-136, and the resulting codes are matched against Table 18-11 to identify possible filters. Information needed for Fig. 18-137 can be obtained by observing the settling of a slurry sample (Purchas suggests 1 L) in a graduated cylinder. Filter-cake-growth rate (Fig. 18-136) is determined by small-scale leaf or funnel tests as described earlier.

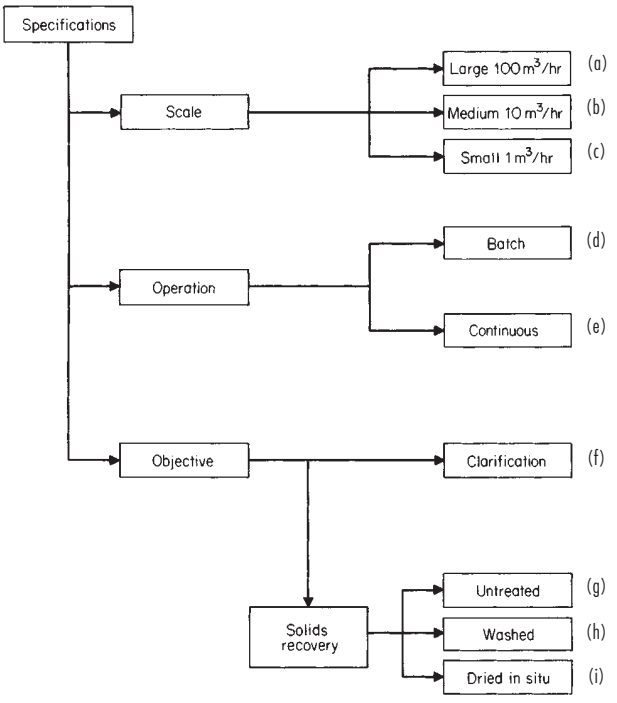


FIG. 18-134 Coding the problem specification. (*Purchas,* Solid/Liquid Separation Equipment Scale-Up, *Uplands Press, Croydon, England, 1977, p. 10, by permission.*)

Almost all types of continuous filters can be adapted for cake washing. The effectiveness of washing is a function of the number of wash displacements applied, and this, in turn, is influenced by the ratio of wash time to cake-formation time. Countercurrent washing, particularly with three or more stages, is usually limited to horizontal filters, although a two-stage countercurrent wash sometimes can be applied on a drum filter handling freely filtering material, such as crystallized salts. Cake washing on batch filters is commonly done, although, generally, a greater number of wash displacements may be required in order to achieve the same degree of washing obtainable on a continuous filter.

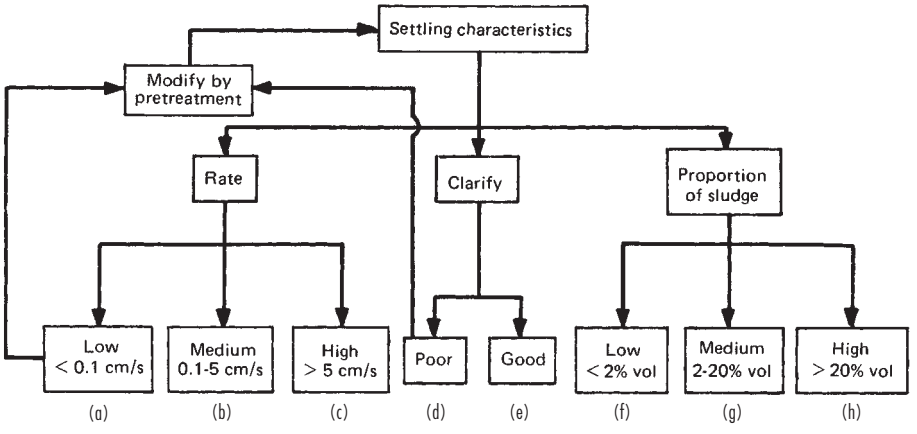


FIG. 18-135 Coding the settling characteristics of a slurry. (*Purchas,* Solid/Liquid Separation Equipment Scale-Up, *Uplands Press, Croydon, England, 1977, p. 11, by permission.*)

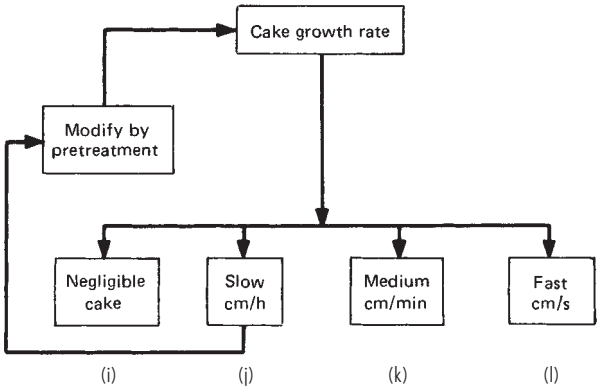


FIG. 18-136 Coding the filtration characteristics of a slurry. (*Purchas, Solid/Liquid Separation Equipment Scale-Up, Uplands Press, Croydon, England, 1977, p. 12, by permission.*)

Continuous filters are most attractive when the process application is a steady-state continuous one, but the rate at which cake forms and the magnitude of production rate are sometimes overriding factors. A rotary vacuum filter, for example, is a dubious choice if a 3-mm (0.12-in) cake will not form under normal vacuum in less than 5 min and if less than 1.4 m^3/h (50 ft^3/h) of wet cake is produced. Upper production-rate limits to the practicality of batch units are harder to establish, but any operation above 5.7 m^3/h (200 ft^3/h) of wet cake should be considered for continuous filtration if it is at all feasible. Again, however, other factors such as the desire for flexibility or the need for high pressure may dictate batch equipment.

For estimating filtration rate (therefore, operating pressure and size of the filter), washing characteristics, and other important features, small-scale tests such as the leaf or pressure bomb tests described earlier are usually essential. In the conduct and interpretation of such tests, and for advice on labor requirements, maintenance schedule, and selection of accessory equipment the assistance of a dependable equipment vendor is advisable.

TABLE 18-11 Classification of Filters According to Duty and Slurry-Separation Characteristics*

Type of equipment	Suitable for duty specification†	Required slurry-separation characteristics‡	
		Slurry-settling characteristics	Slurry-filtering characteristics
Deep-bed filters	a or b	A	T
	e	D	
	f	F	
Cartridges	b or c	A or B	
	d	D or E	
	f	F	
Batch filters			
Pressure vessel with vertical elements	a, b, or c	A or B	I or J
	d	D or E	
	f, g, h, or i	F or G	
Pressure vessel with horizontal elements	b or c	A or B	J or K
	d	D or E	
	g or h	F or G	
Filter presses	a, b, or c	A (or B)	I or J
	d	D or E	
	f, g, h, or i	F, G, or H	
Variable-volume filters	a, b, or c	A (or B)	J or K
	d or e	D or E	
	g (or h)	G or H	
Continuous filters			
Bottom-fed drum or belt drum	a, b, or c	A or B	I, J, K, or L
	e	D or E	
	f, g, h, or i	F, G, or H	
Top-fed drum	a, b, or c	C	L
	e	E	
	g, i (or h)	G or H	
Disk	a, b, or c	A or B	J or K
	e	D or E	
	g	G or H	
Horizontal belt, pan, or table	a, b, or c	A, B, or C	J, K, or L
	d or e	D or E	
	g or h	F, G, or H	

*Adapted from Purchas, *Solid/Liquid Separation Equipment Scale-Up*, Uplands Press, Croydon, England, 1977, p. 13, by permission.
†Symbols are identified in Fig. 18-135.
‡Symbols are identified in Figs. 18-136 and 18-137.

FILTER PRICES

As indicated, one of the factors affecting the selection of a filter is total cost of carrying out the separation with the selected machine. An important component of this cost item is the installed cost of the filter, which starts with the purchase price.

From a survey of early 1982, prices of a number of widely used types of process filter were collated by Hall and coworkers [*Chem. Eng.*, **89**(7), 80 (1982)]. These data are drawn together in Fig. 18-137, updated to 1995 prices. They have a claimed accuracy of ±10 percent, but they should be used confidently only with study-level cost estimations (±25 percent) at best. Cost of delivery to the plant can be approximated as 3 percent of the FOB price [Pikulik and Diaz, *Chem. Eng.*, **84**(21), 106 (1977)].

The cost of the filter station includes not only the installed cost of the filter itself but also that of all the accessories dedicated to the filtration operation. Examples are feed pumps and storage facilities, precoat tanks, vacuum systems (often a major cost factor for a vacuum filter station), and compressed-air systems. The delivered cost of the accessories plus the cost of installation of filter and accessories generally is of the same order of magnitude as the delivered filter cost and commonly is several times as large. Installation costs, of course, must be estimated with reference to local labor costs and site-specific considerations.

The relatively high prices of pulp and paper filters reflect the construction features that accommodate the very high hydraulic capacity that is required. The absence of data for some common types of filters, in particular the filter press, is explained by Hall as due to the complex variety of individual features and materials of construction. For information about missing filters and for firmer estimates for those types presented, vendors should be consulted. In all cases of serious interest, consultation should take place early in the evaluation procedure so that it can yield timely advice on testing, selection, and price.

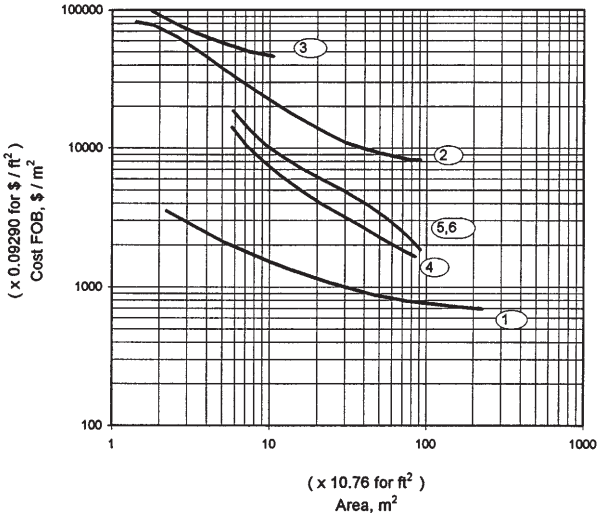


FIG. 18-137 Price of filters installed, FOB point of manufacture. (*EIMCO Process Equipment Co.*)

CENTRIFUGES

General References: Ambler, in McKetta, *Encyclopedia of Chemical Processing and Design,* vol. 7, Marcel Dekker, New York, 1978; also in Schweitzer, *Handbook of Separation Techniques for Chemical Engineers,* McGraw-Hill, New York, 1979, sec. 4. Ambler and Keith, in Perry and Weissberger, *Separation and Purification Techniques of Chemistry,* 3d ed., vol. 12, Wiley, New York, 1978. Flood, Porter, and Rennie, *Chem. Eng.,* **73**(13), 190 (1966). Greenspan, *J. of Fluid Mech.,* **127**(9), 91 (1983). Hultsch and Wilkesmann, in Purchas, *Solid/Liquid Separation Equipment Scale-Up,* Uplands Press, Croydon, England, 2d ed., 1986, chap. 12. Gerl, Stadager, and Stahl, *Chemical Eng. Progress,* **91,** 48–54, (May 1995). Leung, *Chem. Eng.* (1990). Leung, *Fluid-Particle Sep. J.,* **5**(1), 44 (1992). Leung, *10th Pittsburgh Coal Conf. Proceed.* (1993). Leung and Shapiro, *Filtration and Separation Journal,* Sept. and Oct. 1996. Leung and Shapiro, U.S. Patents 5,520,605 (May 28, 1996), 5,380,266 (Jan. 10, 1995), and 5,401,423 (March 28 1995). Mayer and Stahl, *Aufbereitungs-Technik,* **11,** 619 (1988). Moyers, *Chem. Eng.,* **73**(13), 182 (1966). Records, in Purchas, op. cit., chap. 6. Smith, *Ind. Eng. Chem.,* **43,** 439 (1961). Sullivan and Erikson, ibid., p. 434. Svarovsky, in *Solid-Liquid Separation,* 3d ed., Butterworths, 1990, chap. 7. Tiller, *AICHE J.,* **33**(1), (1987). Zeitsch, in Svarovsky, op. cit., chap. 14.

Nomenclature

Symbol	Definition	SI units	U.S. customary units
a	Acceleration	m/s^2	ft/s^2
B_o	Bond number	Dimensionless	Dimensionless
b	Basket axial length	m	ft
C_f	Frictional coefficient	Dimensionless	Dimensionless
D	Bowl/basket diameter	m	in
d	Particle diameter	m	ft
Ek	Ekman number	Dimensionless	Dimensionless
F	Cumulative fraction	Dimensionless	Dimensionless
G	Centrifugal gravity	m/s^2	ft/s^2
g	Earth gravity	m/s^2	ft/s^2
h	Cake height	m	ft
K	Cake permeability	m^2	ft^2
L	Length	m	ft
M	Mass	kg	lb
m	Bulk mass rate	kg/s	lb/h
N_c	Capillary number	Dimensionless	Dimensionless
P	Power	kw	hp
Q	Flow rate	L/s	gpm
R_m	Filter media resistance	m^{-1}	ft^{-1}
Ro	Rossby number	Dimensionless	Dimensionless
r	Radius	m	ft
Rec	solids recovery	Dimensionless	Dimensionless
S	Liquid saturation in cake (=volume of liquid/ volume cake void)	Dimensionless	Dimensionless
sg	Specific gravity	Dimensionless	Dimensionless
t	Time	s	s
t_d	Time	Dimensionless	Dimensionless
u	Velocity	m/s	ft/s
$V\theta$	Circumferential velocity	m/s	ft/s
V_c	Bulk cake volume	m^3	ft^3
V	Velocity	m/s	ft/s
W	Weight fraction of solids	Dimensionless	Dimensionless
Y	Yield	Dimensionless	Dimensionless
Z	Capture efficiency	Dimensionless	Dimensionless
	Greek symbols		
ε	Cake void volume fraction	Dimensionless	Dimensionless
ε_s	Cake solids volume fraction	Dimensionless	Dimensionless
μ	Liquid viscosity	Pa·s	P
ρ_s	Solid density	kg/m^3	lb/ft^3
ρ_L	Liquid density	kg/m^3	lb/ft^3
σ	Surface tension	N/m	lbf/ft
σ_h	Hoop stress	Pa	psi
θ	Angle	Radian	degree
Σ	Scale-up factor (equivalent sedimentation area)	m^2	ft^2
ξ	Time	Dimensionless	Dimensionless

Nomenclature (*Concluded*)

Symbol	Definition	SI units	U.S. customary units
	Greek symbols (Cont.)		
ϕ	Feed solids volume fraction	Dimensionless	Dimensionless
τ_y	Yield stress	Pa	psi
Δ	Differential speed	1/s	r/min
Ω	Angular speed	1/s	r/min
	Subscripts		
b	Bowl or basket		
c	Cake		
e	Centrate		
f	Feed		
f	Filtrate		
acc	Acceleration		
p	Pool		
con	Conveyance		
t	Tangential		
L	Liquid		
s	Solid		

INTRODUCTION

Centrifuges for the separation of solids from liquids are of two general types: (1) sedimenting centrifuges, which require a difference in density of the two phases (solid-liquid or liquid-liquid) and (2) filtering centrifuges (for solid-liquid separation), in which the solid phase is retained by the filter medium through which the liquid phase is free to pass. The following discussion is focused on solid-liquid separation for both types of centrifuges; however, a dispersed liquid phase in another continuous liquid phase as used in sedimenting centrifuges exhibits similar behavior as solid in liquid, and therefore the results developed are generally applicable. The use of centrifuges covers a broad range of applications, from separation of fine calcium carbonate particles of less than 10 μm to coarse coal of 0.013 m (½ in).

GENERAL PRINCIPLES

Centripetal and Centrifugal Acceleration A centripetal body force is required to sustain a body of mass moving along a curve trajectory. The force acts perpendicular to the direction of motion and is directed radially inward. The centripetal acceleration, which follows the same direction as the force, is given by the kinematic relationship:

$$a = \frac{V_\theta^2}{r} \tag{18-75}$$

where V_θ is the tangential velocity at a given point on the trajectory and r is the radius of curvature at that point. This analysis holds for the motion of a body in an inertial reference frame, for example, a stationary laboratory. It is most desirable to consider the process in a centrifuge, and the dynamics associated with such, in a noninertial reference frame such as in a frame rotating at the same angular speed as the centrifuge. Here, additional forces and accelerations arise, some of which are absent in the inertial frame. Analogous to centripetal acceleration, an observer in the rotating frame experiences a centrifugal acceleration directed radially outward from the axis of rotation with magnitude:

$$a = \Omega^2 r \tag{18-76}$$

where Ω is the angular speed of the rotating frame and r is the radius from the axis of rotation.

Solid-Body Rotation When a body of fluid rotates in a solid-body mode, the tangential or circumferential velocity is linearly proportional to radius:

$$V_\theta = \Omega r \tag{18-77}$$

as with a system of particles in a rigid body. Under this condition, the magnitude of the centripetal acceleration, Eq. (18-75), equals that of the centrifugal acceleration, Eq. (18-76), despite the fact that these accelerations are considered in two different reference frames. Hereafter, the rotating frame attached to the centrifuge is adopted. Therefore, centrifugal acceleration is exclusively used.

G-Level Centrifugal acceleration G is measured in multiples of earth gravity g:

$$\frac{G}{g} = \frac{\Omega^2 r}{g} \tag{18-78}$$

With the speed of the centrifuge Ω in r/min and D the diameter of the bowl,

$$\frac{G}{g} = 0.000559\Omega^2 D,\ D(m) \tag{18-79}$$

With D in inches, the constant in Eq. (18-79) is 0.0000142. G can be as low as 100g for slow-speed, large basket units to as much as 10,000g for high-speed, small decanter centrifuges and 15,000g for disk centrifuges. Because G is usually very much greater than g, the effect due to earth's gravity is negligible. In analytical ultracentrifuges used to process small samples, G can be as much as 500,000g to effectively separate two phases with very small density difference.

Coriolis Acceleration The Coriolis acceleration arises in a rotating frame, which has no parallel in an inertial frame. When a body moves at a linear velocity u in a rotating frame with angular speed Ω, it experiences a Coriolis acceleration with magnitude:

$$a = 2\Omega u \tag{18-80}$$

The Coriolis vector lies in the same plane as the velocity vector and is perpendicular to the rotation vector. If the rotation of the reference frame is anticlockwise, then the Coriolis acceleration is directed 90° clockwise from the velocity vector, and vice versa when the frame rotates clockwise. The Coriolis acceleration distorts the trajectory of the body as it moves rectilinearly in the rotating frame.

Effect of Fluid Viscosity and Inertia The dynamic effect of viscosity on a rotating liquid slurry as found in a sedimenting centrifuge is confined in very thin fluid layers, known as **Ekman layers.** These layers are adjacent to rotating surfaces which are perpendicular to the axis of rotation, such as bowl heads, flanges, and conveyor blades, etc. The thickness of the Ekman layer δ is of the order

$$\delta = \sqrt{\frac{(\mu/\rho)}{\Omega}} \tag{18-81}$$

where μ/ρ is the kinematic viscosity of the liquid. For example with water at room temperature, μ/ρ is 1×10^{-6} m^2/s and for a surface rotating at $\Omega = 3000$ r/min, δ is 0.05 mm! These layers are very thin; nevertheless, they are responsible for transfer of angular momentum between the rotating surfaces to the fluid during acceleration and deceleration. They worked together with the larger-scale inviscid bulk flow transferring momentum in a rather complicated way. This is demonstrated by the teacup example in which the content of the cup is brought to speed when it is stirred and it is brought to a halt after undergoing solid-body rotation. The viscous effect is characterized by the dimensionless Ekman number:

$$\mathrm{Ek} = \frac{\mu/\rho}{\Omega L^2} \tag{18-82}$$

where L is a characteristics length. It measures the scale of the viscous effect to that of the bulk flow.

The effect of fluid inertia manifests during abrupt change in velocity of the fluid mass. It is quantified by the Rossby number:

$$\mathrm{Ro} = \frac{u}{\Omega L} \tag{18-83}$$

Typically, Ro is small to the order of 1 with the high end of the range showing possible effect due to inertia, whereas the Ek number is usually very small, 10^{-6} or smaller. Therefore, the viscous effect is confined to thin boundary layers with thickness $\mathrm{Ek}^{1/2}L$.

Sedimenting and Filtering Centrifuges Under centrifugal force, the solid phase assumed to be denser than the liquid phase settles out to the bowl wall—sedimentation. Concurrently, the lighter, more buoyant liquid phase is displaced toward the smaller diameter—flotation. This is illustrated in Fig. 18-138*a*. Some centrifuges run with an air core, i.e., with free surface, whereas others run with slurry filled to the center hub or even to the axis in which pressure can be sustained.

In a sedimenting centrifuge, the separation can be in the form of **clarification,** wherein solids are separated from the liquid phase in which clarity of the liquid phase is of prime concern. For biological sludge, polymers are used to agglomerate fine solids to facilitate clarification. Separation can also be in the form of **classification** and degritting at which separation is effected by means of particle size and density. Typically, the finer solids (such as kaolin) of smaller size and/or density in the feed slurry are separated in the centrate stream as product (for example 90 percent of particles less than 1 μm, etc.), whereas the larger and/or denser solids are captured in cake as reject. Furthermore, separation can be in the form of **thickening,** where solids settle under centrifugal force to form a stream with concentrated solids. In **dewatering** or **deliquoring,** the objective is to produce dry cake with high solids consistency by centrifugation.

In a filtering centrifuge, separating solids from liquid does not require a density difference between the two phases. Should a density difference exist between the two phases, sedimentation is usually at a much more rapid rate compared to filtration. In both cases, the solid and liquid phases move toward the bowl under centrifugal force. The solids are retained by the filter medium, while the liquid flows through the cake solids and the filter. This is illustrated in Fig. 18-138*b*.

Performance Criteria Separation of a given solid-liquid slurry is usually measured by the purity of the separated liquid phase in the centrate (or liquid effluent) in sedimenting mode or filtrate in filtering mode, and the separated solids in the cake. In addition, there are other important considerations. Generally, a selected subset of the following criteria are used, depending on the objectives of the process:

Cake dryness or moisture content
Total solids recovery
Polymer dosage
Size recovery and yield
Volumetric and solids throughput
Solid purity and wash ratio
Power consumption

Cake Dryness In dewatering, usually the cake needs to be as dry as possible. Cake dryness is commonly measured by the solids fraction by weight W or by volume ε_s. The moisture content is measured by the complement of W or ε_s. The volume fraction of the pores and void in the wet cake is measured by the cake porosity $\varepsilon(= 1 - \varepsilon_s)$; whereas the volume fraction of the liquid in the pores of the cake is measured by the saturation S. For well-defined solids in the cake with solid density (bone dry) ρ_s and liquid density ρ_L, and given that the cake volume V_c

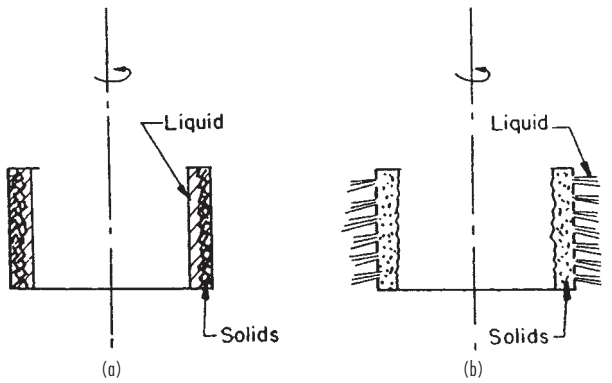


FIG. 18-138 Principles of centrifugal separation and filtration: (*a*) sedimentation in rotating imperforate bowl; (*b*) filtration in rotating perforate basket.

and the mass of solids in the cake w_s are known, the cake porosity is determined by

$$\varepsilon = 1 - \frac{w_s}{\rho_s V_c} \tag{18-84}$$

For undersaturated cake with $S < 1$, saturation can be inferred from the weight fraction of solids and the porosity of the cake, together with the solid and liquid densities:

$$S = \left(\frac{1-W}{W}\right)\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\rho_s}{\rho_L} \tag{18-85}$$

When the cake is saturated $S = 1$, the cake porosity can be determined from Eq. (18-86) as

$$\varepsilon = \left(1 + \frac{\rho_L}{\rho_s}\frac{W}{1-W}\right)^{-1} \tag{18-86}$$

Cake dewatering by compression and rearrangement of the solids in the cake matrix reduce ε, yet the cake is still saturated with $S = 1$. (Assuming cake solids are ideal spheres of uniform size, the maximum packing, in rhombohedral arrangement, is such that $\varepsilon_s = 74$ percent or $\varepsilon = 26$ percent.) Drainage of liquid within the cake by centrifugation further reduces S to be less than 1. There is a lower limit on S which is determined by the cake height, dewatering time, centrifugal force as compared to the capillary and surface forces, as well as the surface roughness and porosity of the particles.

Total Solids Recovery In clarification, the clarity of the effluent is measured indirectly by the total solids recovered in the cake as

$$\text{Rec} = \frac{m_c W_c}{m_f W_f} \tag{18-87}$$

where subscripts c and f denote, respectively, the cake and the feed. m is the bulk mass flow rate in kg/s (lb/h).

Under steady state, the mass balance on both solids and liquid yield, respectively:

$$m_f W_f = m_c W_c + m_e W_e \tag{18-88}$$

$$m_f = m_c + m_e \tag{18-89}$$

From the above, it follows that

$$\text{Rec} = \frac{1 - (W_e/W_f)}{1 - (W_e/W_c)} \tag{18-90}$$

where subscript e represents liquid centrate. Stringent requirements on centrate quality or capture of valuable solid product often require the recovery to exceed 90 percent and, in some cases, 99+ percent. In such cases, the centrate solids are typically measured in ppm.

Polymer Dosage Cationic and anionic polymers have been commonly used to coagulate and flocculate fine particles in the slurry. This is especially pertinent to biological materials such as are found in wastewater treatment. In the latter, cationic polymers are often used to neutralize the negative-charge ions left on the surface of the colloidal particles. Polymer dosage is measured by kg of dry polymer/1000 kg of dry solids cake (lbm of dry polymer/ton of dry solids cake). With liquid polymers, the equivalent (active) dry solid polymer is used to calculate the dosage. There is a minimum polymer dosage to agglomerate and capture the fines in the cake. Overdose can be undesirable to recovery and cake dryness. The range of optimal dosage is dictated by the type of solids in the slurry, slurry physical properties such as pH, ionic strength, etc., and the operating condition and characteristics of the centrifuge. It is known that flocculated particles or flocs obtained from certain polymers may be more sensitive to shear than others, especially during feed acceleration in the centrifuges. A more gentle feed accelerator is beneficial for this type of polymer. Also, polymers can be introduced to the feed at various locations either within or external to the centrifuge.

Size Recovery and Yield Centrifuges have been applied to classify polydispersed fine particles. The size distribution of the particles is quantified by the cumulative weight fraction F less than a given particle size d for both the feed and the centrate streams. It is measured by a particle size counter which operates based on principles such as sedimentation or optical scattering.

In kaolin classification, the product is typically measured with a certain percentage less than a given size (example 90 percent or 95 percent less than 1 or 2 μm). Each combination of percent and size cut represents a condition by which the centrifuge would have to tune to yield the product specification.

The yield Y is defined as the fraction of feed particles of a given size below which they report to the centrate product. Thus,

$$Y = \frac{m_e W_e F_e}{m_f W_f F_f} \tag{18-91}$$

From material balance, the particle size distribution of the feed and centrate, as well as the total solids recovery, determine the yield,

$$Y(d) = \frac{F_e(d)}{F_f(d)}(1 - \text{Rec}) \tag{18-92}$$

The complementary is the cumulative capture efficiency $Z\ (= 1 - Y)$, which is defined as the feed particles of a given size and smaller which are captured in the cake, which in most dewatering applications is the product stream.

Volumetric and Solids Throughput The maximum volumetric and solids throughput to a centrifuge are dictated by one or several governing factors, the most common ones are the centrate solids, cake dryness, and capacity (torque and power) of drive/gear unit. The solids throughput is also governed by other factors such as solids conveyance and discharge mechanisms for continuous and batch centrifuges. The settling rate, as may be significantly reduced by increasing feed solids concentration, also becomes crucial to solids throughput, especially if it has to meet a certain specification on centrate quality.

Solid Purity and Wash Ratio Cake washing is used to remove impurities in cake solids. It is most effective with filtering centrifuges; however, washing can also be done on some sedimenting centrifuges. The wash ratio is defined as the volumetric amount of wash liquid per unit void volume in the cake or per cake solids amount if the cake porosity is not available. Wash ratio of 0.5:4 is typical, depending on the effectiveness of the wash. Separation and repulping also proves to be effective in removing dissolved contaminants in the cake.

Power Consumption Power is consumed to overcome windage and bearing (and seal) friction, to accelerate feed stream from zero speed to full tangential speed at the pool so as to establish the required G-force for separation, and to convey and discharge cake. The power to overcome windage and bearing friction is usually established through tests for a given centrifuge geometry at different rotation speeds. It is proportional to the mass of the centrifuge, to the first power of the speed for the bearing friction, and to the second power of speed for windage. It is also related to the bearing diameter. The seal friction is usually small.

The horsepower for feed acceleration is given by

$$P_{\text{acc}} = 5.984(10^{-10})\text{sg}Q(\Omega r_p)^2 \tag{18-93}$$

where sg is the specific gravity of the feed slurry, Q the volumetric flow rate of feed in gpm(l/s), Ω the speed in r/min, r_p in meters corresponds to the radius of the pool surface for sedimenting centrifuge, or to the radius of the cake surface for filtering centrifuge. *Note:* To convert horsepower to kilowatts, multiply by 0.746.

The horsepower for cake conveyance for scroll centrifuge is

$$P_{\text{con}} = 1.587\ (10^{-5})\ T\Delta \tag{18-94}$$

where Δ is the differential speed in r/min (s^{-1}) between the scroll conveyor and the bowl, and T is the conveyance torque in in·lb_f (N·m). For centrifuge where cake is discharged differently, the conveyance power is simply

$$P_{\text{con}} = MGC_fV \tag{18-95}$$

where M is the mass of the cake, G the centrifugal acceleration, C_f is the coefficient of friction, and V is the cake velocity. Comparing Eqs. (18-94) and (18-95) the conveyance torque is inversely related to the differential speed and directly proportional to the G acceleration, cake velocity, and cake mass.

Stress in the Centrifuge Rotor The stress in the centrifuge rotor is quite complex. Analytical methods, such as the finite element

method, are used to analyze the mechanical integrity of a given rotor design. Without getting into an involved analysis, some useful knowledge can be gained from a simple analysis of the hoop stress of a rotating bowl under load. At equilibrium, the tensile hoop stress σ_h of the cylindrical bowl wall with thickness t is balanced by the centrifugal body force due to the mass of the bowl wall with density ρ_m and its contents (cake or slurry or liquid) with equivalent density ρ_L. Consider a circular wall segment with radius r, unit subtended angle, and unit axial length. A force balance requires

$$\sigma_h = \rho_m V_t^2 \left[1 + 0.5 \frac{\rho_L}{\rho_m} \left(1 - \frac{r_s^2}{r_b^2} \right) \frac{r_b}{t} \right] \tag{18-96}$$

$V_t = \Omega r_b$ is the tip speed of the bowl. The term in the bracket is typically of order 1. If the maximum allowed σ_h is designed to be no more than 60 percent of the yield stress of the bowl material, which for steel is about $2.07(10^8)$ $Nm^{-2}(30{,}000$ $lb_f/in^2)$. Given that the ρ_m of stainless steel is 7867 kg/m^3 (0.284 lbm/in^3), and there is no liquid load, then $(V_t)_{max} = \{\sigma_h/\rho_m\}^{1/2} = 126$ m/s (412 ft/s). With additional liquid load, $\rho_L = 1000$ kg/m^3 (0.0361 lbm/in^3), $r_b/t = 10$, and further assuming the worst case with liquid filling to the axis, the term in the curly bracket is 1.636. Using Eq. (18-96), $(V_t)_{max} = \{\sigma_h/\rho_m/1.636\}^{1/2} = 98$ m/s (322 ft/s). Indeed, almost all centrifuges are designed with top rim speed about 91 m/s (300 ft/s). With special construction materials for the rotor, such as Ferralium, with higher yield stress, the maximum rim speed under full load can be over 122 m/s (400 ft/s).

G-Force vs. Throughput The G-acceleration can be expressed as

$$G = \Omega^2 r_b = \frac{(V_t)_{max}^2}{r_b} \tag{18-97}$$

Figure 18-139 shows the range of diameter of commercial centrifuges and the range of maximum G developed in each type. It demonstrates an inverse relationship between G and r_b at $V_t = (V_t)_{max}$, which is constant for a given material. Figure 18-140 shows a log-log plot of G versus Ω for various bowl diameters, [Eq. (18-97)]. Also, the limiting conditions as delineated by $G = \Omega^2 R = \Omega (V_t)_{max}$ with various $(V_t)_{max}$, are superimposed on these curves. These two sets of curves dictate the operable speed and G for a given diameter and a given construction material for the bowl. The throughput capacity of a machine, depending on the process need, is roughly proportional to the nth power of the bowl radius,

$$Q = C_1 r_b^n \tag{18-98}$$

where n is normally between 2 to 3, depending on clarification, classification, thickening, or dewatering. Thus,

$$G = c_2 (V_t)_{max}^2 Q^{1/n} \tag{18-99}$$

where c_1 and c_2 are constants. It follows that large centrifuges can deliver high flow rate but separation is at lower G-force; vice versa, smaller centrifuges can deliver lower flow rate but separation is at higher G-force. Also, using higher-strength material for construction

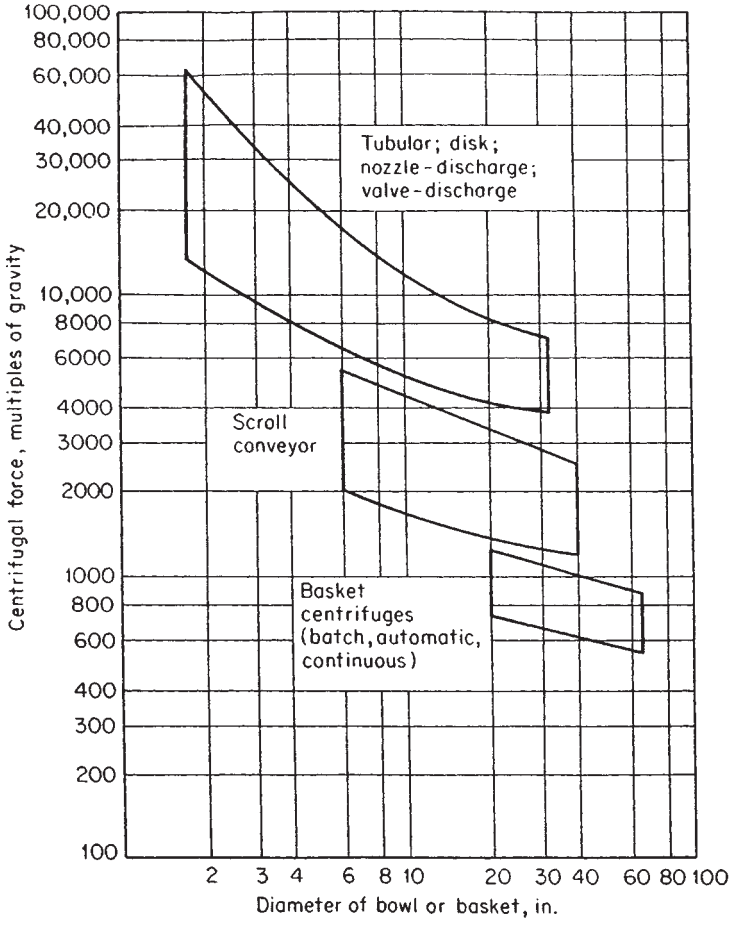


FIG. 18-139 Variation of centrifugal force with diameter in industrial centrifuges.

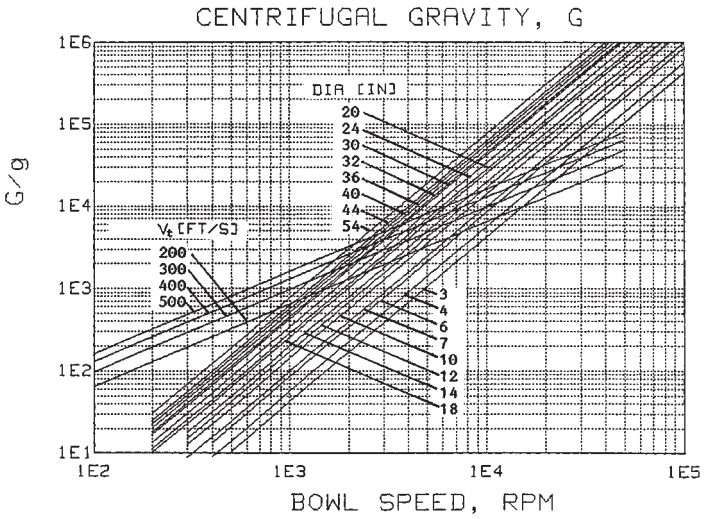


FIG. 18-140 Variation of centrifugal force with r/min.

of the rotating assembly permits higher maximum tip speed, thus allowing higher *G*-force for separation at a given feed rate.

Centrifuge bowls are made of almost every machinable alloy of reasonably high strength. Preference is given to those alloys having 1 percent elongation to minimize the risk of cracking at stress-concentration points. Typically, the list includes carbon steel, types 304, 316, and 317 stainless steels, alloy 20 (Carpenter) stainless steel, Monel Metal, Inconel, nickel, Hastelloy B, titanium, and alloyed aluminum. Vertical-basket centrifuges are frequently constructed of carbon steel or stainless steel coated with rubber, neoprene, Penton, or Kynar. Casings and feed, rinse, and discharge lines that are stationary and lightly stressed may be constructed of any suitable rigid corrosion-resistant material. Wear-resistant materials—tungsten and cermaic carbide, hard-facing, and others—are often used to protect the bare metal surfaces in high-wear areas such as the blade tips of the decanter centrifuge.

Critical Speeds In the design of any high-speed rotating machinery, attention must be paid to the phenomenon of critical speed. This is the speed at which the frequency of rotation matches the natural frequency of the rotating part. At this speed, any vibration induced by slight unbalance in the rotor is strongly reinforced, resulting in large deflections, high stresses, and even failure of the equipment. Speeds corresponding to harmonics of the natural frequency are also critical speeds but give relatively small deflections and are much less troublesome than the fundamental frequency. The critical speed of simple shapes may be calculated from the moment of inertia; with complex elements such as a loaded centrifuge bowl, it is best found by tests.

Nearly all centrifuges operate at speeds well above the primary critical speed and therefore must pass through this speed during acceleration and deceleration. To permit them to do so safely, some degree of damping in their mounting must be provided. This may result from the design of the spindle or driveshaft alone, spring-loading of the spindle bearing nearest the rotor, elastic loading of the suspension, or a combination of these. Smaller and medium-sized centrifuges of the cream-separator and bottle-centrifuge design are frequently mounted on elastic cushions. Horizontal decanter centrifuges are mounted on isolators with dampers to reduce vibration transmitted to the foundation.

SEDIMENTING CENTRIFUGES

When a spherical particle of diameter d settles in a viscous liquid under earth gravity g, the terminal velocity V_s is determined by the weight of the particle-balancing buoyancy and the viscous drag on the particle in accordance to Stokes' law. In a rotating flow, Stokes' law is modified by the "centrifugal gravity" $G = \Omega^2 r$, thus

$$V_s = \frac{1}{18\mu}\Omega^2 r(\rho_s - \rho_L)d^2 \qquad (18\text{-}100)$$

In order to have good separation or high settling velocity, a combination of the following conditions is generally sufficient:

1. High centrifuge speed
2. Large particle size
3. Large density difference between solid and liquid
4. Large radius
5. Small viscosity

Among the five parameters, the settling velocity is very sensitive to change in speed and particle size. It varies as the square of both parameters. The rotation speed can be increased to the limit as dictated by the maximum stress of the rotor or the periphery equipment, such as gear unit. If the particles in the slurry are too small, coagulation and flocculation by polymers is very effective to build up bigger particles for settling. Large density difference leads to higher settling rate and vice versa. Unlike separation under a constant gravitational field, the settling velocity under a centrifugal field increases linearly with the radius. The greater the radius at which separation takes place, the better is the separation. Sedimentation of particles is favorable in a less viscous liquid. Some processes are run under elevated temperature where liquid viscosity drops to a fraction of its original value at room temperature.

Laboratory Tests

Spin-Tube Tests The objective of the spin-tube test is to check the settleability of solids in a slurry under centrifugation. The clarity of the supernatant liquid and the solid concentration in the sediment can also be evaluated. A small and equal amount of feed is introduced into two diametrically opposite test tubes (typically plastic tubes in a stainless steel holder) with a volume of 15 to 50 mL. The samples are centrifuged at a given G and for a period of time t. The supernatant liquid is decanted off from the spin tubes from which the clarity (in the form of turbidity or any measurable solids, dissolved and suspended) is measured. The integrity—more precisely, the yield stress—of the cake can be determined approximately by the amount of penetration of a rod into the cake under its weight and accounting for the buoyancy effect due to the wet cake. It is further assumed that the rod does not lean on the sides of the tube. The yield stress τ_y of the centrifuged cake can be determined from:

$$\tau_y = \frac{1}{2}\left(\frac{\rho_r L}{h} - \rho_L\right) g r_d \tag{18-101}$$

where r_d and L are, respectively, the radius and length of the solid circular rod; ρ_r is the density of the rod; and h is the penetration of the rod into the cake. By using rods of various sizes and densities, yield stress which is indicative of cake handling and integrity can be measured for a wide range of conditions.

The solids recovery in the cake can be inferred from measurements using Eq. (18-90). It is shown as a function of G-seconds for different feed solids concentration in Fig. 18-141; see also theory discussed below.

Imperforate Bowl Tests The amount of supernant liquid from spin tubes is usually too small to warrant accurate gravimetric analysis. A fixed amount of slurry is introduced at a controlled rate into a rotating imperforate bowl to simulate a continuous sedimentation centrifuge. The liquid is collected as it overflows the ring weir. The test is stopped when the solids in the bowl build up to a thickness which affects centrate quality. The solid concentration of the centrate is determined similarly to that of the spin tube.

Transient Centrifugation Theory As in gravitational sedimentation, there are three layers which exist during batch settling of a slurry in a centrifuge: a clarified liquid layer closest to the axis, a middle feed slurry layer with suspended solids, and a cake layer adjacent to the bowl wall with concentrated solids. Unlike with constant gravity g, the centrifugal gravity G increases linearly with radius. It is highest near the bowl and is zero at the axis of rotation. Also, the cylindrical surface area through which the particle has to settle increases linearly with radius. Both of these effects give rise to some rather unexpected results.

Consider the simple initial condition $t = 0$ where the solid concentration ϕ_{so} is constant across the entire slurry domain $r_L \le r \le r_b$ where r_L and r_b are, respectively, the radii of the slurry surface and the bowl. At a later time $t > 0$, three layers coexist: the top clarified layer, a middle slurry layer, and a bottom sediment layer. The air-liquid interface remains stationary at radius r_L, while the liquid-slurry interface with radius r_s expands radially outward, with t with r_s given by:

$$\frac{r_s}{r_L} = \sqrt{\frac{\phi_{so}}{\phi_s}} \tag{18-102}$$

Eq. (18-102) can be derived from conservation of angular momentum as applied to the liquid-slurry interface.

Interestingly, the solid concentration in the slurry layer ϕ_s does not remain constant with time as in gravitational sedimentation. Instead, ϕ_s decreases with time uniformly in the entire slurry layer in accordance to:

$$\frac{\phi_s}{\phi_{smax}} = 1 - \left[1 - \left(\frac{\phi_{so}}{\phi_{smax}}\right)\right] e^{2\xi} \tag{18-103}$$

where ξ is a dimensionless time variable:

$$\xi = \left(\frac{V_{go} t}{r_b}\right)\left(\frac{G}{g}\right) \tag{18-104}$$

In Eqs. (18-103) and (18-104), under hindered settling and 1 g, the solids flux $\phi_s V_s$ is assumed to be a linear function of ϕ_s decreasing at a rate of V_{go}. Also, the solids flux is taken to be zero at the "maximum" solids concentration ϕ_{smax}. As $G/g >> 1$, this solids flux behavior based on 1 g is assumed to be ratioed by G/g.

Concurrent with the liquid-slurry interface moving radially outward, the cake layer builds up with the cake-slurry interface moving radially inward, with radial position given by:

$$\frac{r_c}{r_b} = \sqrt{\frac{(\varepsilon_s - \phi_{so})}{(\varepsilon_s - \phi_s)}} \tag{18-105}$$

where ε_s is a constant cake solids concentration. Sedimentation stops when the growing cake-slurry interface meets the decreasing slurry-liquid interface with $r_c = r_s$. This point is reached at $\phi_s = \phi_s^*$ and $t = t^*$ when

$$\frac{1}{\phi_s^*} = \frac{1}{\varepsilon_s} + \left(\frac{r_b}{r_L}\right)^2 \left(\frac{1}{\phi_{so}} - \frac{1}{\varepsilon_s}\right) \tag{18-106}$$

$$t^* = \frac{1}{2}\left(\frac{g r_b}{G V_{go}}\right) \ln\left(\frac{\phi_{smax} - \phi_s^*}{\phi_{smax} - \phi_{so}}\right) \tag{18-107}$$

Example

Calcium carbonate–water slurry

$G/g = 2667$

$V_{go} = 1.31 \times 10^{-6}$ m/s (5.16×10^{-5} in/s)

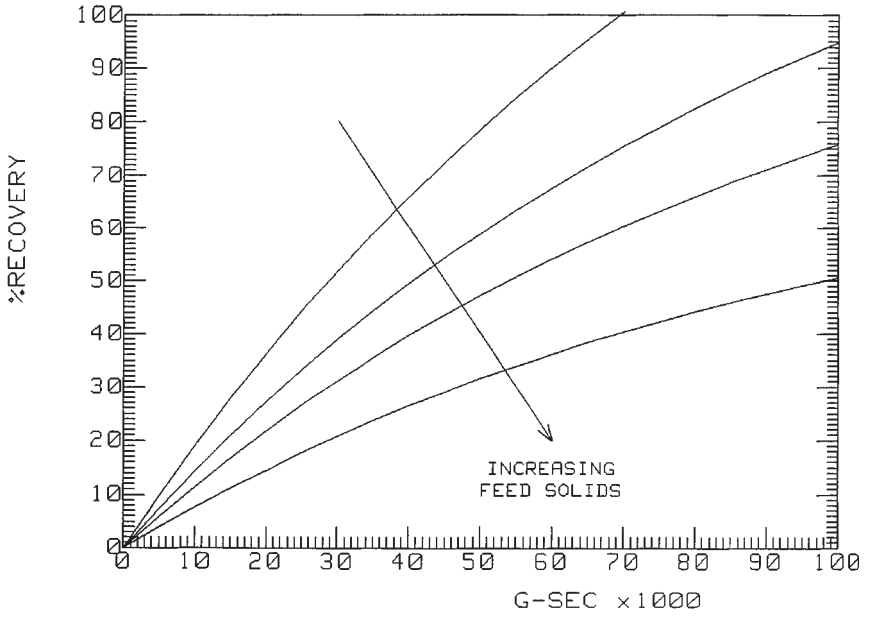


FIG. 18-141 Recovery as a function of G-seconds for centrifugal sedimentation.

$\phi_{smax} = 0.26$ (with $\phi_s V_g = 0$)
$\phi_{so} = 0.13$
$r_L = 0.0508$ m (2 in)
$r_b = 0.1016$ m (4 in)
$\xi = 2667\ (1.31 \times 10^{-6})\ (1/0.1016) = 0.0344$
$\varepsilon_s = 0.52$

$t(s)$	ξ	ϕ_s/ϕ_{smax}	r_s (m)	r_c (m)
0.0	0	0.50	0.051	0.102
1.0	0.034	0.46	0.053	0.100
5.0	0.173	0.29	0.067	0.095
7.6	0.261	0.16	0.091	0.091

There are six types of industrial sedimenting centrifuges:
Tubular-bowl centrifuges
Multichamber centrifuges
Skimmer pipe/knife-discharge centrifuges
Disk centrifuges
Decanter centrifuges
Screenbowl centrifuges
The first three types, including the manual-discharge disk, are batch-feed centrifuges, whereas the latter three, including the intermittent and nozzle-discharge disks, are continuous centrifuges.

Tubular-Bowl Centrifuges The tubular-bowl centrifuge is widely employed for purifying used lubricating and other industrial oils and in the food, biochemical, and pharmaceutical industries. Industrial models have bowls 102 to 127 mm (4 to 5 in) in diameter and 762 mm (30 in) long (Table 18-12). It is capable of delivering up to 18,000*g*. The smallest size, 44 mm × 229 mm (1.75 in × 9 in bowl), is a laboratory model capable of developing up to 65,000*g*. It is also used for separating difficult-to-separate biological solids with very small density difference, such as cells and virus.

The bowl is suspended from an upper bearing and drive (electric or turbine motor) assembly through a flexible-drive spindle with a loose guide in a controlled damping assembly at the bottom. The unit finds its axis of rotation if it becomes slightly unbalanced due to process load.

The feed slurry is introduced into the lower portion of the bowl through a small orifice. Immediately downstream of the orifice is a distributor and a baffle assembly which distribute and accelerate the feed to circumferential speed. The centrate discharges from the top end of the bowl by overflowing a ring weir. Solids that have sedimented against the bowl wall are removed manually from the centrifuge when the buildup of solids inside the bowl is sufficient to affect the centrate clarity.

The liquid-handling capacity of the tubular-bowl centrifuge varies with use. The low end shown in Table 18-11 corresponds to stripping small bacteria from a culture medium. The high end corresponds to purifying transformer oil and restoring its dielectric value. The solids-handling capacity of this centrifuge is limited to 4.5 kg (10 lb) or less. Typically, the feed stream solids should be less than 1 percent in practice.

Multichamber Centrifuges While the tubular has a high aspect ratio (i.e., length-to-diameter ratio) of 5 to 7, the multichamber centrifuges have aspect ratios of 1 or less. The bowl driven from below consists of a series of short tubular sections of increasing diameter nested to form a continuous tubular passage of stepwise increasing diameter for the liquid flow. The feed is introduced at the center tube and gradually finds its way to tubes with larger diameters. The larger and denser particles settle out in the smaller-diameter tube, while the smaller and lighter particles settle out in the larger-diameter tubes. Classification of particles can be conveniently carried out. Clarification may be significantly improved by spacing especially the outer tubes more closely together to reduce the settling distance, a concept which is fully exploited by the disk-centrifuge design. This also serves to maintain a constant velocity of flow between adjacent tubes. As much as six chambers can be accommodated. The maximum solids-holding capacity is 0.064 m^3 (17 gal). The most common use is for clarifying fruit juices, wort, and beer. For these services it is equipped with a centripetal pump at effluent discharge to minimize foaming and contact with air.

Knife-Discharge Centrifugal Clarifiers Knife-discharge centrifuges with solid instead of perforated bowls are used as sedimenting

TABLE 18-12 Specifications and Performance Characteristics of Typical Sedimenting Centrifuges

Type	Bowl diameter	Speed, r/min	Maximum centrifugal force × gravity	Throughput		Typical motor size, hp
				Liquid, gal/min	Solids, tons/h	
Tubular	1.75	50,000*	62,400	0.05–0.25		*
	4.125	15,000	13,200	0.1–10		2
	5	15,000	15,900	0.2–20		3
Disk	7	12,000	14,300	0.1–10		⅓
	13	7,500	10,400	5–50		6
	24	4,000	5,500	20–200		7½
Nozzle discharge	10	10,000	14,200	10–40	0.1–1	20
	16	6,250	8,900	25–150	0.4–4	40
	27	4,200	6,750	40–400	1–11	125
	30	3,300	4,600	40–400	1–11	125
Helical conveyor	6	8,000	5,500	To 20	0.03–0.25	5
	14	4,000	3,180	To 75	0.5–1.5	20
	18	3,500	3,130	To 100	1–3	50
	24	3,000	3,070	To 250	2.5–12	125
	30	2,700	3,105	To 350	3–15	200
	36	2,250	2,590	To 600	10–25	300
	44	1,600	1,600	To 700	10–25	400
	54	1,000	770	To 750	20–60	250
Knife discharge	20	1,800	920	†	1.0‡	20
	36	1,200	740	†	4.1‡	30
	68	900	780	†	20.5‡	40

*Turbine drive, 100 lb/h (45 Kg/h) of steam at 40 lbf/in^2 gauge (372 KPa) or equivalent compressed air.
†Widely variable.
‡Maximum volume of solids that the bowl can contain, ft^3.
NOTE: To convert inches to millimeters, multiply by 25.4; to convert revolutions per minute to radians per second, multiply by 0.105; to convert gallons per minute to liters per second, multiply by 0.063; to convert tons per hour to kilograms per second, multiply by 0.253; and to convert horsepower to kilowatts, multiply by 0.746.

centrifuges. The liquid flow is usually continuous until the settled solids start to interfere with the effluent liquid. The feed enters the hub end and is accelerated to speed before introducing to the separation pool. The solids settle out to the bowl wall and the clarified liquid overflows the ring weir or discharges through a skimmer pipe. In some designs, internal baffles in the bowl are required to stop wave action primarily along the axial direction. When sufficient thick solid layer has built up inside the bowl, the supernatant liquid is skimmed off by moving the opening of the skimmer pipe radially inward. After the liquid is sucked out, the solids are knifed out as with centrifugal filters. However, unlike centrifugal filters, the cake is always fully saturated with liquid, $S = 100\%$. These centrifuges are used for coarse, fast-settled solids. When greater clarification effectiveness is required, the operation may be totally batchwise with prolonged spinning of each batch. If the solids content in the feed is low, several batches may be successively charged and the resulting supernatant liquor skimmed off before unloading of the accumulated solids.

Commercial centrifuges of this type have bowl diameters ranging from 0.3 to 2.4 m (12 to 96 in). The large sizes are used on heavy-duty applications such as coal dewatering and are limited by stress considerations to operate at 300*g*. The intermediate sizes for chemical process service develop up to 1000*g* (see Table 18-10).

Disk Centrifuges One of the commonest clarifier centrifuges is the vertically mounted disk machine, as illustrated in Fig. 18-142*a*, *b*. Feed is introduced proximate to the axis of the bowl, accelerated to speed typically by a radial vane assembly, and flows through a stack of closely spaced conical disks in the form of truncated cones. Generally 50 to 150 disks are used. They are spaced 0.4 to 3 mm (0.015 to 0.125 in) apart to reduce the distance for solid/liquid separation. The angle made by conical disks with the horizontal is typically between 40 to 55° to facilitate solids conveyance. Under centrifugal force the solids settle against the underside of the disk surface and move down to the large end of the conical disk and subsequently to the bowl wall. Concurrently, the clarified liquid phase moves up the conical channel. Each disk carries several holes spaced uniformly around the circumference. When the disk stack is assembled, the holes provide a continuous upward passage for the lighter clarified liquid released from each conical channel. The liquid collects at the top of the disk stack and discharges through overflow ports. To recover the kinetic energy and avoid foaming due to discharging of a high-velocity jet against a stationary casing, the rotating liquid is diverted to a stationary impeller from which the kinetic energy of the stream is converted to hydrostatic pressure. Unlike most centrifuges operating with a slurry pool in contact with a free surface, disk centrifuges with a rotary seal arrangement can operate under high pressure. The settled solids at the bowl wall are discharged in different forms, depending on the type of disk centrifuges.

Manual Discharge Disk Centrifuges In the simplest design shown in Fig. 18-142*a*, the accumulated solids must be removed manually on a periodic basis, similar to that for the tubular-bowl centrifuge. This requires stopping and disassembling the bowl and removing the disk stack. Although the individual disks rarely require cleaning, manual removal of solids is economical only when the fraction of solids in the feed is very small.

Intermittent-Discharge Disk Centrifuges In the intermittent-discharge-disk centrifuge, solids discharge through ports at the periphery of the bowl, the ports opening on a timed cycle while the bowl is at speed. In another design, the bottom of the bowl drops, exposing an annular opening where accumulated solids are discharged. The bowl closes and the cycle repeats.

Nozzle-Discharge Disk Centrifuges In the nozzle-discharge disk centrifuge, solids are discharged continuously, along with a portion of the liquid phase, through nozzles spaced around the periphery of the bowl, which are tapered radially outward, providing a space for solids storage (see Fig. 18-142*b*). The angle of repose of the sedimented solids determines the slope of the bowl walls for satisfactory operation. Clarification efficiency is seriously impaired if the buildup of solids between nozzles reaches into the disk stack. The nozzle diameter should be at least twice the diameter of the largest particle to be processed, and prescreening is recommended of extraneous solids. Typically, nozzle diameters range from 0.6 to 3 mm (0.25 to 0.125 in). Large disk centrifuges may have as much as 24 nozzles spaced out at the bowl.

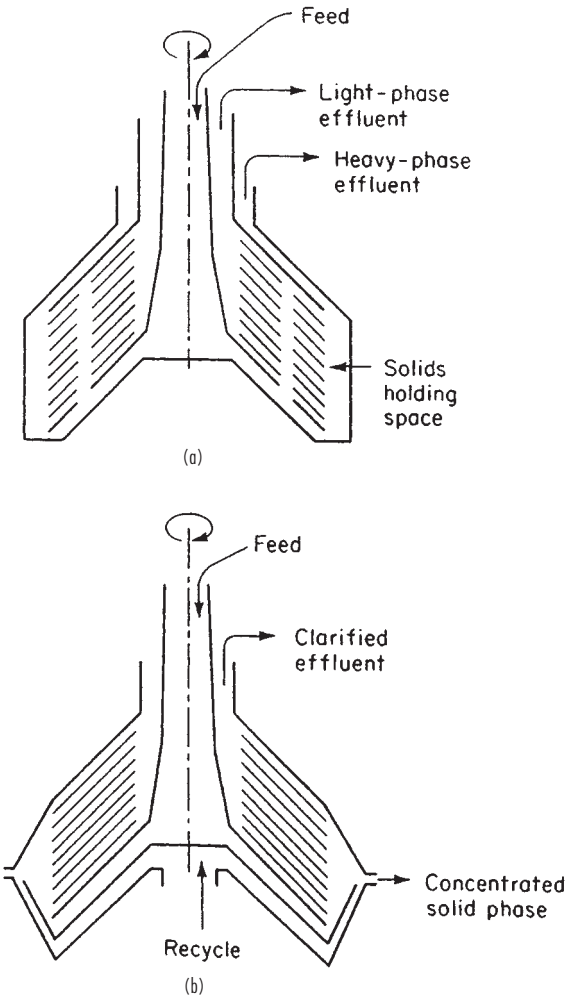


FIG. 18-142 Disk-centrifuge bowls: (*a*) separator, solid wall; (*b*) recycle clarifier, nozzle discharge.

For clarification of a single liquid phase with controlled concentration of the discharged slurry, a centrifuge which provides recirculation is used (see Fig. 18-142*b*). A fraction of the sludge discharged out of the machine is returned to the bowl to the area adjacent to the nozzles through lines external to the machine as well as built-in annular passages at the periphery of the bowl. This has the effect of preloading the nozzles with sludge which has already been separated and reduces the net flow of liquid with the newly sedimented solids from the feed. Increased concentration can be obtained alternatively by recycling a portion of the sludge to the feed, but this increases solids loading at the disk stack, with a corresponding sacrifice in the effluent clarity for a given feed rate.

With proper rotary seals, the pressure in the machine can be contained up to 1.1 MPa (150 psig) or higher. Also, operating temperature can be as high as 315°C (about 600°F). The rotating parts are made of stainless steel with the high-wear nozzles made of tungsten carbide. The bowls may be underdriven or suspended and range from several centimeters to over 1 m (3.3 ft) in outer diameter. The largest size capable of clarifying up to 1920 L/m (500 gpm) requires 112 kW (150 hp).

Decanter Centrifuges The decanter centrifuge (also known as the **solid-bowl** or **scroll** centrifuge) consists of a solid bowl with a

screw or scroll conveyor between the solid- and the liquid-bowl heads, or hubs (see Fig. 18-143). Both the bowl and the conveyor rotate at a high speed, yet there is a difference in speed between the two, which is responsible for conveying the sediment along the machine from the cylinder to the conical discharge end. The rotating assembly is commonly mounted horizontally with bearings on each end. Some centrifuges are vertically mounted with the weight of the rotating assembly supported by a single bearing at the bottom or with the entire machine suspended from the top. With the former configuration, the weight of the rotating assembly provides a good sealing surface at the bearing for high-pressure applications. The bowl may be conical in shape or, in most instances, it has combined conical and cylindrical sections (see Fig. 18-143).

Slurry is introduced into the feed accelerator through a stationary pipe located proximate to the axis of the machine. The feed slurry is accelerated through contact with the rotating surfaces to angular speed before discharging to the separation pool through a series of ports in the conveyor hub. In the separation pool, under centrifugal gravity the solids which are heavier compared to the liquid settle toward the bowl wall, while the clarified liquid moves radially toward the pool surface. Subsequently, the liquid flows along the helical channel (or channels, if the screw conveyor has multiple leads) formed by adjacent blades of the conveyor to the liquid bowl head, from which it discharges over the weirs. The annular pool can be changed by adjusting the radial position of the weir openings, which take the form of circular holes or crescent-shaped slots.

The cake solids adjacent to the bowl wall are transported by the differential speed from the cylinder up the cone, also known as the **beach.** The half cone angle ranges between 5° and 20°. The cake is submerged in the pool when it is in the cylinder and at the beginning of the beach. In this region, liquid buoyancy helps to reduce the effective weight of the cake under centrifugal gravity, resulting in lower conveyance torque. Farther up the beach, the cake emerges above the pool and moves along the "dry beach," where buoyancy force is absent, resulting in more difficult conveyance and higher torque. But it is also in this section that the cake is dewatered, with expressed liquid returned back to the pool. The centrifugal force helps to dewater, yet at the same time hinders the transport of the cake in the dry beach. Therefore, a balance in cake conveyance and cake dewatering is the key in setting the pool and the *G*-force for a given application. Also, clarification is important in dictating this decision.

The cylindrical section provides clarification under high centrifugal gravity. In some cases, the pool should be shallow to maximize the *G*-force for separation. In other cases, when the cake layer is too thick inside the cylinder, the settled solids—especially the finer particles at the cake surface—entrain into the fast-moving liquid stream above, which eventually ends up in the centrate. A slightly deeper pool becomes beneficial in these cases because there is a thicker buffer liquid layer to ensure settling of resuspended solids. This can be at the expense of cake dryness due to reduction of the dry beach. Consequently, there is again a compromise between centrate clarity and cake dryness. Another reason for the tradeoff of centrate clarity with cake dryness is that, in losing fine solids to the centrate (i.e., classification), the cake with larger particles, having less surface-to-volume ratio, can dewater more effectively, resulting in drier cake. It is best to determine the optimal pool for a given application through tests.

The speed with which the cake transports is controlled by the differential speed. High differential speed facilitates high solids throughput where the cake thickness is kept to a minimum so as not to impair centrate quality due to entrainment of fine solids. Also, cake dewatering is improved due to a reduction in the drainage path with smaller cake height; however, this is offset by the fact that higher differential speed also reduces cake residence time, especially in the dry beach. The opposite holds for low differential speed. Therefore, an optimal differential speed is required to balance centrate clarity and cake dryness. The desirable differential speed is usually maintained using a two-stage planetary gearbox, the housing of which rotates with the bowl speed, with a fixed first-stage pinion shaft. In some applications, the pinion is driven by an electrical backdrive (dc or ac), hydraulic backdrive, or braked by an eddy-current device at a fixed rotation speed. The differential speed is then the difference in speed between the bowl and the pinion divided by the gear ratio. This also applies to the case when the pinion arm is held stationary, in which the pinion speed is zero. The torque at the spline of the conveyor, conveyance torque, is equal to the product of the pinion torque and the gear ratio. Higher gear ratio gives lower differential speed, and vice versa; lower gear ratio gives higher differential for higher solids capacity. The torque at the pinion shaft has been used to control the feed rate or to signal an overload condition by shearing of a safety pin. Under this condition, both the bowl and the conveyor are bound to rotate at the same speed (zero differential) with no conveyance torque and no load at the pinion.

Soft solids, most of which are biological waste such as sewage, are difficult to convey up the beach. Annular baffles or dams have been commonly used to provide a pool-level difference wherein the pool is deeper upstream of the baffle toward the clarifier and lower downstream of the baffle toward the beach. The pool-level difference across the baffle, together with the differential speed, provide the driving force to convey the compressible sludge up the beach. This has been used effectively in thickening of waste-activated sludge and in some cases of fine clay with dilatant characteristics.

High solids decanter centrifuges have been used to dewater mixed raw sewage sludge (with volume ratio of primary to waste-activated sludge such as 50 percent to 50 percent or 40 percent to 60 percent, etc.), aerobically digested sludge, and anaerobically digested sludge.

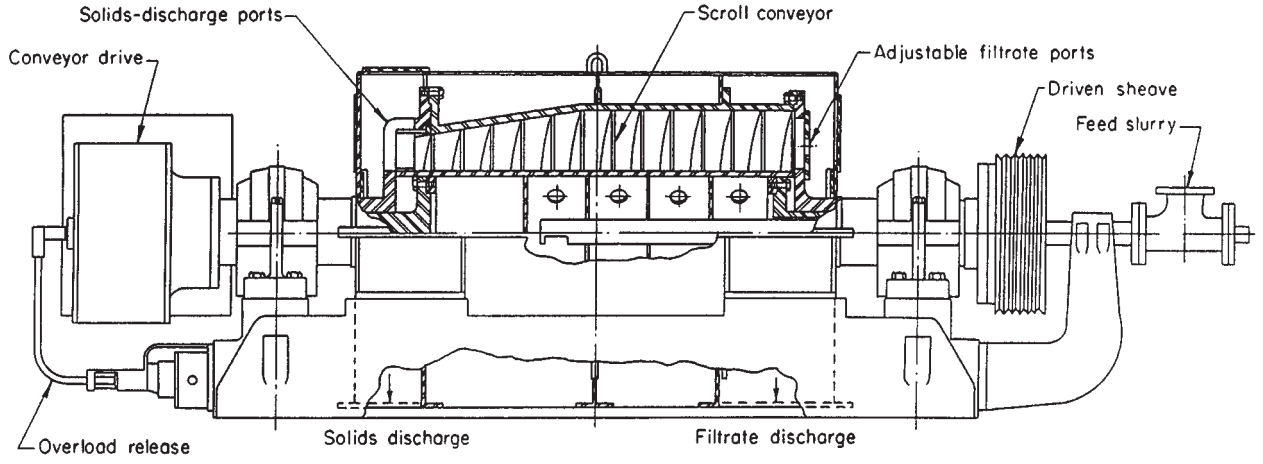


FIG. 18-143 Cylindrical-conical solid-bowl centrifuge. (*Bird Machine Co.*)

Cake solids as dry as 28 percent to 35 percent by weight are obtained for raw mixed sludge and 20 percent to 28 percent for the digested sludges, with the aerobic sludge at the lower end of the range. The typical characteristics of high-solids applications are: low differential speed (0.5 to 3 r/min), high conveyance torque, high polymer dosage (10 to 30 lb dry polymer/ton dry solids, depending on the feed sewage), and slightly lower volumetric throughput rate. An electrical (dc or ac with variable-frequency drive) or hydraulic backdrive on the conveyor with high torque capacity is essential to operate these conditions at steady state.

The horizontal decanter centrifuge is operated below its critical speed. The bowl is mounted between fixed bearings anchored to a rigid frame. The gearbox is cantilevered outboard of one of these bearings, and the feed pipe enters the rotating assembly through the other end. Particularly in the larger sizes, the frame is connected to ground through vibration isolators. In the vertical configuration, the bowl and the gearbox are suspended from the drive head, which is connected to the frame and casing through vibration isolators. A clearance bushing at the bottom limits the excursion of the bowl during start-up and shutdown but does not provide the radial constraint of a bearing under normal operating conditions.

Decanter centrifuges with mechanical shaft-to-casing seals are available for pressure containment up to 1.1 MPa (150 psig), similar to the nozzle-disk centrifuge. They can be built to operate at temperatures from –87 to +260°C (–125 to +500°F).

When abrasive solids are processed, the points of wear are protected with a replaceable hard facing such as Colmonoy, Hastelloy, tungsten carbide, or ceramic tiles. These high-wear areas include the feed zone; the conveyor blade tip, especially the pressure or pushing face; the conical beach; and the solids discharge ports. Transport of solids is encouraged in some applications by longitudinal strips or grooves at the inner diameter of the bowl, especially at the beach, to enhance the frictional characteristics between the sediment and the bowl surface, and by polished conveyor faces to reduce frictional drag. For fluidlike sediment cake, by using the strips in the beach, a much tighter gap between the conveyor blade tip and the bowl surface is possible with a cake heel layer trapped by the strips. This reduces leakage of the fluid sediment flowing through an otherwise larger gap opening to the pool. Gypsum coating on the bowl wall at the beach section has been used to achieve the same objective.

Washing in a continuous decanter is fairly effective on solid particles larger than 80 μm (200 mesh), provided the particles are reasonably uniform in size with porous structure. Otherwise, the wash flows across the cake surface with little penetration because the pores at the cake surface are plugged by fines. Rinsing efficiency, the proportion of soluble impurities displaced from the solids, is in the range of 50 to 80 percent, depending on cake porosity, permeability, and mass-transfer rate. A wash-solids weight ratio of up to 0.25 is required.

Various bowl configurations with a wide range of aspect ratios—i.e., length-to-diameter ratio—from less than 1 to 4 are available for specific applications, depending on whether the major objective is maximum clarification, classification, or solids dryness. Generally, the movement of liquid and solids is in countercurrent directions, but in the cocurrent design the movement of liquid is in the same direction as that of the solids. In this design, the feed is introduced at the large end of the machine and the centrate is taken by a skimmer at the beach-cylinder junction. The settled solids transverse the entire machine and discharge at the beach exit. Compound angle beaches are used in specific applications such as washing and drying of polystyrene beads. The pool level is located at the intersection of the two angles at the beach, the steeper angle being under the pool and the shallower angle above the pool (i.e., dry beach), allowing a longer dewatering time. The wash is applied at the pool side of the beach-angle intersection and functions as a continuously replenished annulus of wash liquid through which the solids are conveyed. The size of decanter centrifuge ranges from 6 in diameter to 54 in. The larger is the machine, the slower is the speed, and less is the *G*-force (Fig. 18-141). However, it provides a much higher throughput capacity, which cannot be accommodated with smaller machines (see Table 18-10).

Screenbowl Centrifuges The screenbowl centrifuge consists of a solid-bowl decanter to which, at the smaller conical end, a cylindrical screen has been added (see Fig. 18-144). The scroll spans the entire bowl, conforming to the profile of the bowl. It combines a sedimenting centrifuge together with a filtering centrifuge. Therefore, the solids which are processed are typically larger than 23 to 44 μm.

As in a decanter, an accelerated feed is introduced to the separation pool. The denser solids settle toward the bowl wall and the effluent escapes through the ports at the large end of the machine. The sediment is scrolled toward the beach, typically with a steeper angle compared to the decanter centrifuge. As the solids are conveyed to the screen section, the liquid in the sediment cake further drains through the screen, resulting in drier cake. Washing of the sediment in the first half of the screen section is very effective in removing impurities, with the second half of the screen section reserved for dewatering of mother liquor and wash liquid.

The screen is typically constructed of a wedge-bar with an aperture between adjacent bars, which opens up to a larger radius. This prevents solids from blinding the screen as well as reduces conveyance torque. For abrasive materials such as coal, the screens are made of wear-resistant materials such as tungsten carbide.

Continuous Centrifugal Sedimentation Theory The Stokes settling velocity of a spherical particle under centrifugal field is given

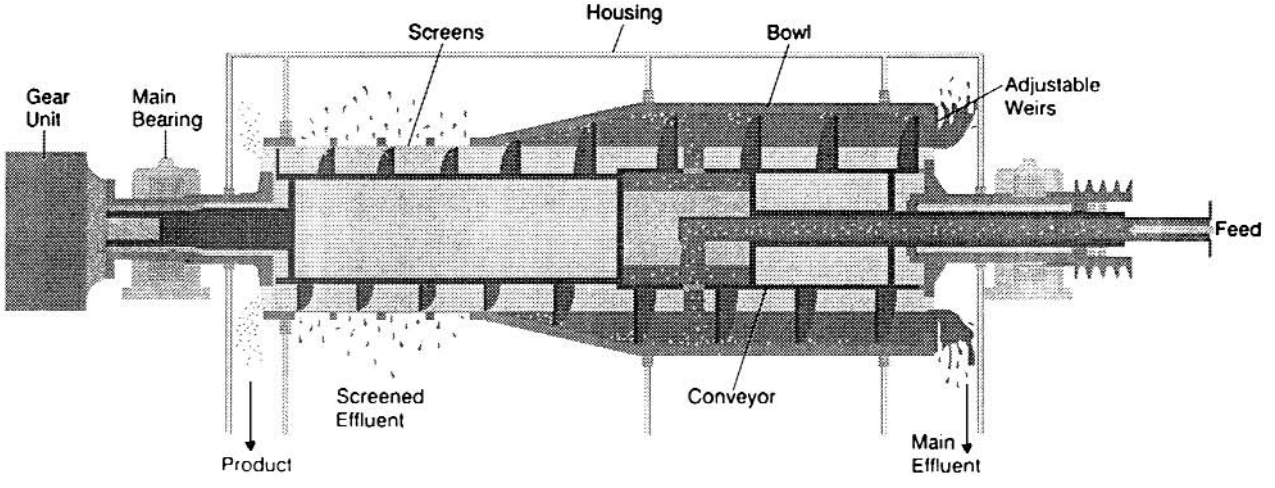


FIG. 18-144 Cylindrical-conical screen-bowl centrifuge. (*Bird Machine Co.*)

by Eq. (18-100). Useful relationships have been established on continuous sedimentation by studying the kinematics of settling of a spherical particle of diameter d in an annular rotating pool. Equating the time rate of change in a radial position to the settling velocity, and the rate of change in an axial position to bulk-flow velocity, thus gives

$$\frac{dr}{dt} = crd^2 \tag{18-108}$$

$$\frac{dx}{dt} = \frac{Q}{\pi (r_b^2 - r_p)} \tag{18-109}$$

where $c = (\rho_s - \rho_L)\ \Omega^2/18\mu$, x is distance along the axis of the bowl, Q is the volumetric feed rate, r_b and r_p are, respectively, the bowl and pool surface radii. For a particle located at one end of the bowl at radius r with $r_p < r < r_b$, after transversing the full bowl length, it settles out and is captured by the bowl wall. Solving the above equations with these boundary conditions, the limiting trajectory is:

$$\frac{r}{r_b} = \exp\left[\frac{-\pi\, cL(r_b^2 - r_p^2)d^2}{Q}\right] \tag{18-110}$$

If the same size particle d is located at an initial starting radius less than r given by Eq. (18-110) it is assumed to escape from being captured by the bowl, whereas it would have been captured if it had been at an initial radius greater than r. Assuming that the number of particles with size d is uniformly distributed across the annular pool, the recovery Rec_d (known also as **grade efficiency**) is the differential of the cumulative recovery $Z = 1 - Y$, with Y given in Eq. (18-92) for particles with size d, as the ratio of the two annular areas:

$$\text{Rec}_d = \frac{r_b^2 - r^2}{r_b^2 - r_p^2} \tag{18-111}$$

Combining Eqs. (18-110) and (18-111), the maximum Q to the centrifuge, so as to meet a given recovery Rec_d of particles with diameter d, is

$$\frac{Q_d}{2V_{gd}} = \left(\frac{\pi\, \Omega^2 L}{g}\right)\left(\frac{r_p^2 - r_b^2}{\ln\{1 - \text{Rec}_d[1 - (r_p/r_b)^2]\}}\right) = \Sigma_{\text{Rec}_d} \tag{18-112}$$

Note in Eq. (18-112) that V_{gd} is the settling rate under 1g, and it is a function of the particle size and density and fluid properties. The ratio $Q_d/2V_{gd}$ is then related only to the operating speed and geometry of the centrifuge, as well as to the size recovery. It measures the *required* surface area for settling under centrifugal gravity to meet a specified Rec_d. When the size recovery Rec_d is set at 50 percent, the general result, Eq. (18-112), reduces to the special case, which is the well-known Ambler's Sigma factor, which for a straight rotating bowl (applicable to bottle centrifuge, decanter centrifuge, etc.) is:

$$\Sigma = \left[\frac{\pi\, \Omega^2 L}{g}\right]\left[\frac{r_b^2 - r_p^2}{\ln\,[2r_b^2/(r_b^2 + r_p^2)]}\right] \tag{18-113}$$

It can be simplified to:

$$\Sigma = \pi\, \Omega^2 L \frac{(3r_b^2 + r_p^2)}{2g} \tag{18-114}$$

For a disk centrifuge, a similar derivation results in

$$\Sigma = \frac{2\pi\, \Omega^2\, (N - 1)\, (r_2^3 - r_1^3)}{3g \tan\theta} \tag{18-115}$$

where N is the number of disks in the stack, r_1 and r_2 are the outer and inner radii of the disk stack, and θ is the conical half-angle.

Typical Σ factors for the three types of sedimenting centrifuges are given in Table 18-13. In scale-up from laboratory tests, sedimentation performance should be the same if the value of Q/Σ is the same for the two machines. This is a widely used criterion for the comparison of centrifuges of similar geometry and liquid-flow patterns developing approximately the same G; however, it should be used with caution when comparing centrifuges of different configurations. In general, the shortcomings of the theory are due to the oversimplified assumptions being made, such as (1) there is an idealized plug-flow pattern; (2) sedimentation abides by Stokes law as extended to many g's; (3) feed solids are uniformly distributed across the surface of the bowl head at one end of the clarifier and capture implies that the particles' trajectory intersect the bowl wall; (4) the feed reaches full tangential speed as it is introduced to the pool; (5) the recovery of given-size particles is at 50 percent; (6) this does not account for possible entrainment of already settled particles in the liquid stream; (7) there is absence of entrance and exit effects.

Experience in using the Σ concept has demonstrated that the calculated Σ factor should be modified by an efficiency factor to account for some of the aforementioned effects which are absent in the theory and, as such, this factor depends on the type of centrifuge. It is nearly 100 percent for simple spin-tube bottle centrifuge, 80 percent for tubular centrifuge, and less than 55 percent for disk centrifuges. The

TABLE 18-13 Scale-up Factors for Sedimenting Centrifuges

Type of centrifuge	Inside diameter, in	Disk diameter, in/number of disks	Speed, r/min	$\sum$ value, units of 10^4 ft^2	Recommended scale-up factors*
Tubular	1.75	—	23,000	0.32	1†
Tubular	4.125	—	15,000	2.7	21
Tubular	4.90	—	15,000	4.2	33
Disk	—	4.1/33	10,000	1.1	1
Disk	—	9.5/107	6,500	21.5	15
Disk	—	12.4/98	6,250	42.5	30
Disk	—	13.7/132	4,650	39.3	25
Disk	—	19.5/144	4,240	105	73
Helical conveyor	6	—	6,000	0.27	1
Helical conveyor	14	—	4,000	1.34	5
Helical conveyor	14‡	—	4,000	3.0	10
Helical conveyor	18	—	3,450	3.7	12.0
Helical conveyor	20	—	3,350	4.0	13.3
Helical conveyor	25	—	3,000	6.1	22
Helical conveyor	25	—	2,700	8.6	31

*These scale-up factors are relative capacities of centrifuges of the same type but different sizes when performing at the same level of separation achievement (e.g., same degree of clarification). These factors must not be used to compare the capacities of different types of centrifuges.

†Approaches 2.5 at rates below mL/min.

‡Long bowl configuration.

NOTE: To convert inches to millimeters, multiply by 25.4; to convert revolutions per minute to radians per second, multiply by 0.105; and to convert 10^4 square feet to square meters, multiply by 929.

efficiency varies widely for decanter centrifuges, depending on cake conveyability and other factors.

FILTERING CENTRIFUGES

As in sedimenting centrifuges, heavier solids settle to the bowl to form a cake layer. In filtering centrifuges, the bowl wall is a screen, a perforated surface, or, in general, a filtering medium. Under a centrifugal field, the liquid above, as well as that trapped in the cake, flows through the cake and the filter. Because the solids are coarser as compared to those processed by sedimenting centrifuges, settling under centrifugal gravity is quick, leaving filtration as the limiting step of the process. Washing and subsequent dewatering of the cake are very common for filtering centrifuges. Filtering centrifuges are also known as centrifugal filters, **wringers, extractors,** or **dryers.** There is a difference in the various types of machines according to whether the feed is batch, intermittent, or continuous, and in the manner in which the cake solids are removed from the basket. The operating range of filtering centrifuges is shown in Table 18-14.

Batch Centrifuges Despite the tendency of the industry to be in favor of continuous filtering centrifuges to reduce downtime and increase productivity, batch-filtering centrifuges still share a significant market due to improvement in modern control and measurement technology, allowing certain operational flexibilities which are unique in the batch machines.

Unlike continuous-filtering centrifuges, the duration and centrifugal gravity for filtration, washing, and final dewatering in batch centrifuges are adjustable. This facilitates qualitative optimization of the processed products and adjustment to varying product requirements. Surge tanks with controlled inlet and a bypass loop permit integration of batch centrifuges into continuous processes.

Variable-Speed Basket Centrifuges A typical cycle of a variable-speed basket centrifuge is shown in Fig. 18-145. The basket accelerates to medium speed, after which feed slurry is introduced. Subsequently, both the slurry and the basket are further accelerated to a higher operating speed. Under the high *G*-force, the cake is washed and spun dry. Afterwards the basket decelerates to a low speed at which the cake is unloaded. The cycle is repeated. The rate of acceleration depends on the inertia of the basket and load, as well as the available torque from the drive; whereas the rate of deceleration depends on the inertia of the rotating mass and the available braking force. The unloading time depends on the torque available for turning the basket at unloading speed, the rheological properties of the cake to be unloaded, and the design of the unloading knife. The remainder of the cycle depends on the processing characteristics of the slurry to be centrifuged—the filtration rate of the mother liquor, the wash and the drain rate of the wash liquor, and the final drying of the cake to a residual moisture level. The operating cycle may be either manual or fully automatic through a sequence of programmed steps employing reset timers, speed sensors, and limit switches.

Variable-speed basket centrifuges rotate on a vertical axis. The cylindrical perforated basket, connected at one end to a bowl head or hub, is driven from below or suspended from above by a driveshaft. It is capped at the other end with a weir ring. The hub may be a solid piece or with an annular opening. If the hub is a solid piece, the slurry is introduced into the basket at low speed despite the fact that the earth's gravity may influence the annular pool. The settled solids can be removed from the top only when the machine is at rest. Otherwise, the feed has to be introduced when the machine is at high rotation speed so that an annular pool forms instantly. With an open bottom, settled solids are removed from the bottom either manually while the basket is at rest or by an unloader knife while the basket is rotating at a low speed of less than 100 r/min. The filter medium can be screen or filter cloth with a support.

Solid-Bottom Basket Centrifuges Smaller-scale, solid-bottom batch basket centrifuges are available for small test samples, when the sample cannot tolerate mechanical handling or when the traces of solids remaining in a more automated centrifuge would be subject to decomposition or spoilage.

Base-Bearing Centrifuges The driveshaft of the centrifuge is supported from below on a thrust bearing, which is often held and pivoted in a ball joint. The shaft is centered by radial springs or rubber in compression. This provides damped freedom of motion of the axis of rotation to compensate for the out-of-balance condition of a basket load. This type of centrifuge is used extensively in **chip wringers** that recover excess oil from metal chips and turnings. The basket wall is usually solid and tapered radially outward toward the top, ending in an annular lid wherein the oil is freely discharged but the chip is withheld. A typical unit is 660 mm (26 in) in diameter at the top and 584 mm (23 in) at the bottom, holds up to 0.15 m^3 (5 ft^3) or about 225 kg (500 lb) of crushed steel chips and is driven at 1025 r/min (370g) by a 7.5-kW (10-hp) motor.

Link-Suspended Basket Centrifuges In centrifuges with diameters larger than 762 mm (30 in), the basket, curb, curb cover, and drive form a rigid assembly flexibly suspended from three fixed posts (also known as a **three-column centrifuge**). The three suspension members may be either chain links or stiff rods in ball-and-socket joints and are spring-loaded. The suspended assembly has restrained freedom to oscillate to compensate for a normal out-of-balance condition. The drive is vertical with more efficient power transmission compared to the base-bearing type.

This type of centrifuge is usually loaded at zero speed. Therefore, loading should be uniform inside the basket, after which the machine is brought up to operating speed and maintained for a period until the free liquid has drained off through an opening in the bottom of the curb. The basket is brought to rest and the cover lid is opened for unloading. This may be facilitated if the filter medium is in the form of a bag contoured to fit the inside of the basket.

Link-suspended centrifuges with solid bottoms are available with inside diameters ranging from 305 to 2743 mm (12 to 108 in).

Open-Bottom Basket Centrifuges These centrifuges are made in top-suspended and link-suspended configurations. In both, the bottom bowl head consists of three functional components contained in a single fabrication: (1) the central nave by which the basket is attached to the driveshaft, (2) an outer ring to which the cylindrical shell is attached and whose inside diameter is less than that of the liquid ring weir on the opposite end of the basket, and (3) spokes connecting the nave to the outer ring. A typical cycle follows that shown in Fig. 18-145. The control of the cycle may be manual, semiautomatic, or fully automatic. The drive may be a variable-speed electric motor, either direct or through V-belts; a high-pressure, fixed-volume hydraulic motor receiving its energy from a constant-speed variable-volume pump; or, infrequently in modern practice, a steam or water turbine.

The unloading may be accomplished manually with a hand-driven plow or knife mounted on the curb cover or automatically with a double- or single-acting knife with hydraulic or pneumatic piston actua-

TABLE 18-14 Operating Range of Filtering Centrifuges

Type of centrifuge	*G*/*g*	Minimum feed solids concentration by wt.	Minimum mean particle size, μm	Minimum V_{fo}, m/s
Vibratory	30–120	50	300	5×10^{-4}
Tumbler	50–300	50	200	2×10^{-4}
Screen scroll	500–2000	35	75	1×10^{-5}
Pusher	300–1200	40	120	5×10^{-5}
Screen bowl	500–2000	20	45	2×10^{-6}
Peeler	300–1600	10	10	2×10^{-7}
Pendulum	200–1200	10	5	1×10^{-7}

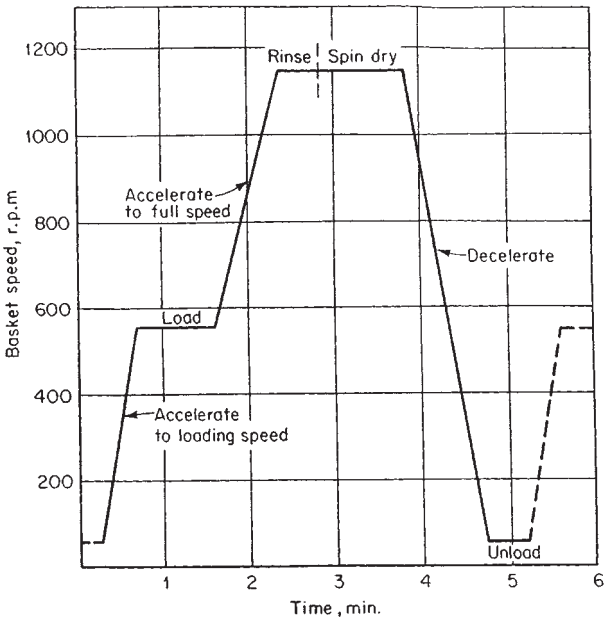


FIG. 18-145 Typical operating cycle, batch-filtering centrifuge.

tors. In some designs, the opening through the basket is covered with a plate which is lifted during unloading.

Top-Suspended Centrifuges The top-suspended centrifuge (also known as a **pendulum centrifuge,** see Fig. 18-146) is widely used for purging molasses from crystallized sugar, as well as for many other applications. Conventionally, the drive is suspended from a horizontal bar supported at both ends from two A-frames. The drive head, which is connected to the motor or a driven pulley through a flexible coupling, carries the thrust and radial bearings that support the shaft and its load. The cylindrical bowl has a ring weir at the top. The stationary casing is attached to the A-frame. The filtrate is collected and diverted to an outlet in the casing.

The entire weight of the motor is carried on the frame with no component of force other than its rotation reacting on the centrifuge proper. This permits the use of very large special motors for rapid cycling. On white-sugar service, up to 24 cycles/h with 364 kg (800 lb) of sugar per load are provided by wound-rotor variable-speed ac motors with a power rating of 112 kW (150 hp).

Typical pilot-plant top-suspended baskets are 305 mm (12 in) diameter by 127 mm (5 in) deep. Commercial machines are available in sizes from 508-mm (20-in) diameter by 305-mm (12-in) depth to 1524-mm (60-in) diameter by 1016-mm (40-in) depth and develop up to 1800*g* in the smaller and intermediate sizes. Except in the sugar application, operation with a two-speed motor (half speed for loading and full speed for purging) is typical. Hydraulic drives with variable-speed capability are commonly used in the chemical industry. To maximize the number of cycles per hour, a combination of electrical and mechanical braking is employed to minimize the deceleration period, which is a transition period of no value to the process.

Link-Suspended Bottom-Discharge Centrifuges With the top-suspended design, the only limit to the size and weight of the drive motor is the strength of the supporting structure, which can be made as strong as possible. With the link-suspended design, the weight of the side-mounted motor constitutes an overturning moment, and therefore this weight is limited to a proportion of the remaining suspending components. For a basket with diameter 1219 mm (48 in) and depth 762 mm (30 in), only a relatively lightweight 45-kW (60-hp) motor is employed. Typically it is a two-speed operation, as with other basket centrifuges—half speed for loading and full speed for deliquoring. Greater torque transmission and more flexibility in speed control are possible with hydraulic drives.

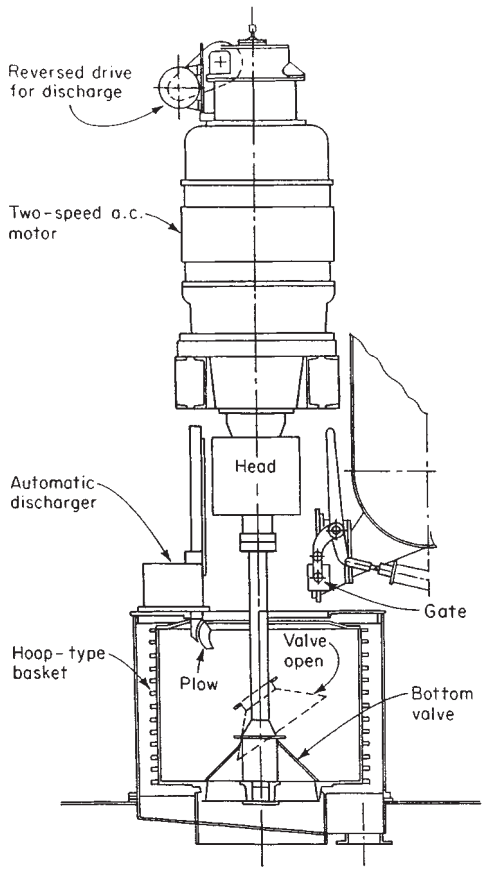


FIG. 18-146 Top-suspended filtering centrifuge. (*Western States Machine Co.*)

Batch-Automatic Basket Centrifuges Some batch centrifuges operate automatically on a preprogrammed cycle and are known as **batch-automatic** or **semiautomatic** centrifugal filters. The peeler, the rotary siphon centrifuge, and the pressurized-siphon centrifuges all belong to this category.

Peeler Centrifuges The peeler centrifuges operate at a constant speed during the entire sequence of feeding, deliquoring, and cake discharging, so that no process time is lost in acceleration and deceleration. All peeler centrifuges operate on a horizontal axis of rotation, with the driveshaft supported by fixed bearings. The basket may be cantilevered at one end of the driveshaft, with the driven pulley at the other end. In another design, the driveshaft extends through the basket and is also supported by an outboard bearing. The through-shaft design may carry two baskets with a common hub to allow feeding one basket while the other is spinning to smooth out the power demand.

A cake distributor may be provided to level the load during feeding, to indicate cake depth, and to activate the feed-valve closure when the desired cake depth has been reached. After the cake has been spun dry, the cake is peeled out by rotating an unloader knife into it to discharge the solids down a chute extending through the opening in the ring weir at the front of the basket. In other designs, the unloader knife is smaller and double-acting, and in very large sizes, the discharge of the cake through the front of the basket is facilitated with a horizontal screw conveyor. Because the unloader knife cannot be allowed to contact the filter medium, a heel of product remains in the basket after each unloading. This serves as a precoat to prevent loss of fines through the screen during the next cycle. The disadvantage is

that it also adds resistance to filtration similar to the filter medium. The heel may become glazed and impervious from the rubbing action of the knife, and a rinse or backwash of the screen is frequently required to restore the permeability.

The peeler centrifuges are used to dewater insoluble solids such as coal, starch, and citric acid gypsum. Their widest application is for dewatering and washing solids such as specialty chemicals, pharmaceuticals, and thermoplastics having medium to fast drain rates, typically 50 to 200 mesh (297 to 74 μm). The drive is usually an electric motor and must be large enough to bring the empty basket to operating speed and also to accelerate the feed slurry. Usually, for optimum performance, the feed rate should match the cake drain rate so that a minimum of free mother liquor is left on the surface of the cake when the feed valve closes. Some modern versions are equipped with gastight design for fume control.

Diameters of the peelers range from 609 mm (24 in) to 1422 mm (56 in) with widths of 406 mm (16 in) to 1422 mm (56 in). The small units can achieve 3000*g*, whereas the large units operate at 1000*g*.

Rotary-Siphon Peeler Centrifuges In this type of centrifuge, a partial vacuum is drawn on the outer diameter of the filter such that the filtrate flows through the cake under both centrifugal force as well as a positive pressure difference of about 1 atm or less. Thus, a higher rate of filtration takes place due to the increased driving force.

In the siphon peeler (Fig. 18-147), the filtrate leaving the basket is collected at the solid bowl. It flows farther axially along the bowl through an annulus to a chamber with a larger diameter as compared to the solid bowl. In this chamber, an annular baffle is used to maintain a difference in liquid head across the baffle. The liquid head is higher upstream toward the basket and is maintained at a lower level downstream by a stationary skimmer tube which opens tangentially along the pool surface. The kinetic energy of the filtrate sustains the liquid to flow through the skimmer tube and connecting tube and into a storage tank. Part of the liquid is returned to the rotating chamber of the centrifuge, whereas the remaining portion overflows the storage tank and exits the system.

The suction pressure generated is equal to the liquid head difference across the annular baffle as magnified by *G*. The maximum suction that can be realized, assuming negligible vapor pressure, is 1 atm. For example, with a differential liquid level of 2 cm (0.79 in) of water across the annulus under 500*g*, the suction generated by the siphon is 0.98 atm.

Pressurized Siphon Basket Centrifuges In addition to a siphoning action downstream of the filter, an additional pressure difference of as much as 5 to 6 atm is imposed across the filter to further enhance dewatering. Usually before the high pressure is imposed, the centrifuge reduces speed so that the cake formed is less compact and the positive pressure gradient provides a better filtration on an otherwise low-permeability centrifuge cake. The basket is pressurized; so is the feed pipe. In one design, the filter is inverted during cake discharge to remove the heel cake left on the filter. In another design, dewatering of the centrifuged cake is enhanced by thermal drying.

Continuous-Filtering Centrifuges The trend toward continuous processing and reduction in labor has resulted in more demanding requirements on continuous-processing equipment, including centrifuges. Despite the elimination of downtime, which translates to lower solids throughput, the continuous centrifuge is less flexible than the batch counterpart because there is no separate control on filtering, dry spinning, washing, and final dewatering for both time and *G*-force, which for different functions may be different for optimal result. There are several types of continuous-filtering centrifuges, the principal distinction among which is the solids conveyance mechanism.

Conical-Screen Centrifuges When a conical screen in the form of a frustum is rotated about its axis, the component of the centrifugal force normal to the screen surface impels the liquid to filter through the cake and the screen, whereas the component of the centrifugal force parallel to the screen in the longitudinal direction conveys the cake to the screen at a larger diameter. The sliding of the solids on the cone is favored by smooth perforated plates or wedge-wire sections with slots parallel to the axis of rotation, rather than woven wire mesh.

Wide-angle conical screen centrifuges. If the half-angle of the cone screen is greater than the angle of repose of the solids, the solids will slide across it with a velocity which depends on frictional properties of the cake but not on feed rate. The frictional property of the cake depends on the solid property, such as shape and size, as well as on moisture content. If the half-angle of the cone greatly exceeds the angle of repose, the cake slides across the screen at a high velocity, thereby reducing the retention time for dewatering. The angle selected is therefore highly critical with respect to performance on a specific application. Wide-angle and compound-angle centrifuges are used to dewater coarse coal and rubber crumb and to dewater and wash crude sugar and vegetable fibers such as from corn and potatoes.

Shallow-angle conical screen centrifuges. By selecting a half-angle for the conical screen that is less than the angle of repose of the cake and providing supplementary means for the controlled conveyance of the cake across the conical screen from the small to large diameter, longer retention time is available for cake dewatering. Three methods are in common use for cake conveyance:

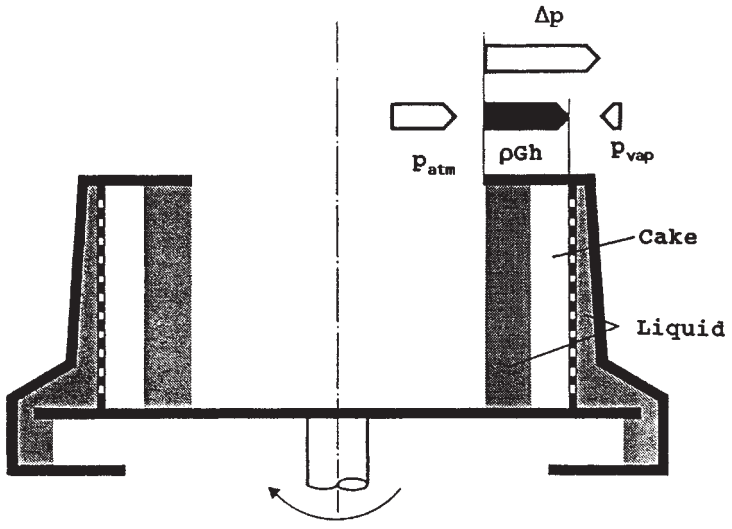


FIG. 18-147 Filtration with a rotary-siphon centrifuge.

1. *Vibrational conveyance.* This is referred as the vibratory centrifuge. A relatively high frequency force is superimposed on the rotating assembly. This can be either in-line with the axis of rotation or torsional, around the driveshaft. In either case, the cake under inertial force from the vibration is partly "fluidized" and propelled down the screen under a somewhat steady pace toward the large end, where it is discharged.

2. *Oscillating or "tumbling" conveyance.* This is commonly known as the tumbling centrifuge. The driveshaft is supported at its lower end on a pivot point. A supplementary power source causes the shaft and the rotating bracket it carries to gyrate about the pivot at a controlled amplitude and at a frequency lower than the rate of rotation of the basket. The inertia force generated also provides partial fluidization of the bed of solids in the basket, causing the cake to convey toward the large end, as in the vibrational conveyance.

3. *Scroll conveyance.* The screen-scroll centrifuge, Fig. 18-148, is the most common shallow-angle conical screen centrifuge. The cake conveyance is controlled by either a continuous helical screw conveyor or with a discrete set of profiled scraper blades, usually in sets of eight. The conveyor guides the cake solids down the conical screen by the differential rotation between the conveyor and the screen. The conveyor is driven by a cyclogear or a gearbox.

The several types of conical-screen centrifuges are constructed with both vertical and horizontal axes of rotation for various applications and installation requirements. Their energy requirement is low, for example, as little as 792 J/kg (0.2 kWh/ton) to dewater −19 +6 mm (−¾ +¼ in) stoker coal at the rate of 38 kg/s (150 ton/h) to 6 percent surface moisture on a large oscillatory centrifuge. The screen-scroll centrifuge can handle finer-size coal with the lower end at 0.5 mm (28 mesh). Their liquid-handling capacity is limited, and 50% feed-slurry concentration is recommended to obtain best performance and capacity. For this reason, the amount of cake wash that can be applied is restricted and, therefore, the wash efficiency is relatively low. As with any filtering centrifuge, performance is also optimized with operation on large and uniformly sized solid particles. Screen thickness, and, hence, screen life, is a function of the openings that will support the solids of the size being centrifuged, the conveyance mechanism, and, finally, whether the feed slurry is accelerated to speed before it lies on the screen at the small diameter. Underaccelerated feed slurry, when introduced to the small conical area, wears out the screen as it slips on the screen surface.

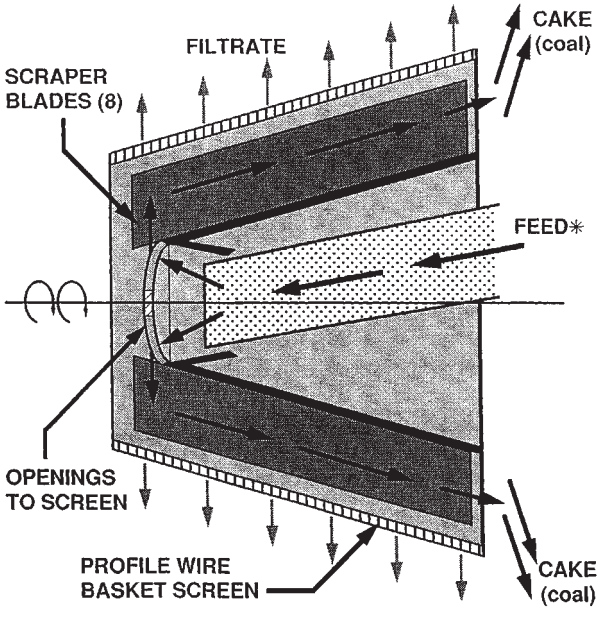


FIG. 18-148 Screen-scroll centrifuge. (*Bird Machine Co.*)

Recently, the performance of the screen-scroll centrifuges benefit from a more effective feed accelerator technology. Not only is the screen wear at the small end of the screen being significantly reduced, the liquid-handling capacity has also increased. For fine coal application, a 900-mm (36-in) diameter centrifuge operating at a speed of 700 r/min used to process 10 to 15 kg/s (40 to 60 ton/h) can handle with a better feed accelerator 20 to 25 kg/s (80 to 100 ton/h), yielding the same cake moisture of 5 percent.

The screen-scroll centrifuge is somewhat more flexible than the others in terms of ability to handle lower feed solids concentration and provide fair to good washing efficiency. This type, together with the wide-angle centrifuge, are used for the dewatering of cellulosic fibers. The screen-scroll centrifuge has also applied to the process crystal form of edible lactose with size 150 to 165 mesh (100 to 240 μm). With a 450-mm (18-in) outer diameter screen, the machine can process 5 ton/h at 50 percent solids. The wash rate is 3.5 to 7×10^{-8} $m^3/s/kg$ (0.5 to 1 gpm/ton). After passing through the centrifuge, the lactose solids are dried to 4 to 8 percent moisture.

Pusher Centrifuges

Single-stage pusher. The pusher centrifuge consists of a rotating, perforated, cylindrical basket lined with wedge-wire screen with the slots parallel to the axis of rotation. The cylinder is open with no ring weir at the solids-discharge end and is cantilevered at the other end through its hub to a hollow driveshaft (Fig. 18-149*a*). Inside the basket and fitting close to the cylindrical screen is an annular pusher plate. This is mounted on its own shaft inside the driveshaft. It rotates at the same speed as the basket and concurrently reciprocates axially via a hydraulic mechanism. The slurry is fed near the centerline of the machine and is distributed and accelerated in the rotating feed chamber, which usually takes the form of a cone or a disk. As the pusher plate retracts, a clean surface of screen is exposed for bulk drainage of the incoming feed slurry. As the pusher plate advances, the incremental annulus of the cake thus formed transmits its "pressure" to the annulus of the cake already in the basket, causing an equivalent amount to discharge out of the basket at the open end. Cake wash is applied as a spray through which the cake advances stepwise. Pusher stroke, usually less than 50 mm (2 in), and stroke rate, usually under 100 cpm, depending on the size of the unit and the load requirement, are usually controllable from outside the machine.

The wedge-bar screen construction minimizes friction between the screen and the advancing cake to permit the use of a relatively long screen and correspondingly long retention time for the cake without buckling.

In one modification, the pusher plate consists of a conical screen with an angle slightly greater than the angle of repose of the cake solids. This accelerates the feed slurry and provides extra area for bulk drainage, permitting operation over a wider range of feed concentrations.

Multistage pusher. In a multistage variation, as shown in Fig. 18-149*b,* the basket consists of a series of concentric stages of baskets that increase in diameter in the direction of solids discharge. The first (smallest-diameter) stage and each alternate stage, which are fixed to the inner shaft, rotate and reciprocate. The final stage (largest-diameter) and alternate stages, which are fixed to the outer shaft, rotate but do not reciprocate. Each screen section is relatively short, with its own pusher action from the preceding stage so that there is less tendency for cake buckling with even a relatively long bowl. Bulk filtration, with liquid above and in the cake, occurs in the small-diameter section with minimum power consumption, and film drainage takes place in the large-diameter section under maximum *G*-force. In one design, the second-stage basket is conical to facilitate cake transport, has a thinner cake layer, and a higher *G*-force toward the solid discharge end.

Single-stage vs. multistage. Below a limiting feed rate, the cake thickness is constant, depending on the length of the basket. The cake advance velocity increases with increasing feed rate. At higher feed rate, the velocity reaches a maximum (stroke frequency × stroke length) and stays constant. Any further increase in feed rate results in a thicker cake at the same maximum conveyance velocity. As the feed rate further increases, it reaches a point at which the feed rate is greater than the bulk filtration rate, resulting in a slurry pool forming above the cake surface, which in effect drives a higher filtration rate due to the extra liquid

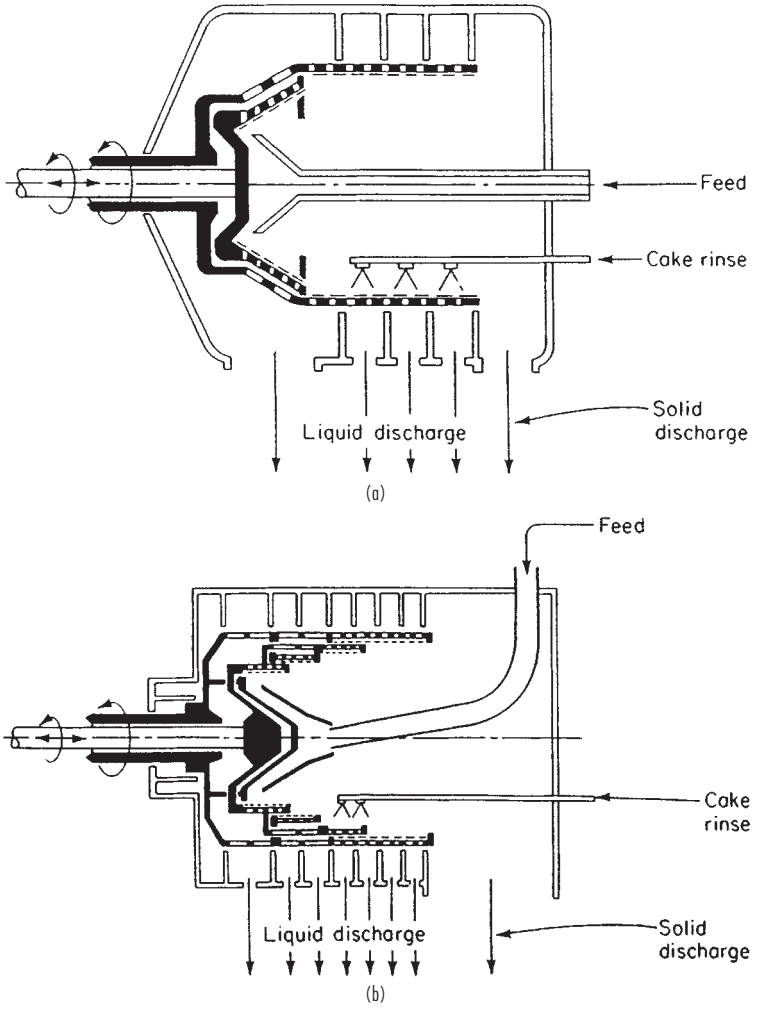


FIG. 18-149 Schematic of pusher centrifuge: (*a*) single-stage pusher; (*b*) multistage pusher.

head. If this increase in filtration rate does not offset the increase in feed rate, a swallowing limit is reached in which the liquid slurry runs over the product cake, which heretofore acts as a dam for the slurry.

Another limit plays a role when the cake at the feed zone has not reached a consistency to be conveyed, in which case it slops over on the preceding cake in the basket. This is especially true for cake which has a low filtration rate. The stroke frequency has to be reduced accordingly.

The velocity of the cake is less than the stroke per unit cycle time, the ratio of which is the **pushing efficiency.** Depending on the moisture of the cake as well as the frictional characteristics of the screen, a 90 percent efficiency can be attained in proper operation.

By having a short basket in each stage for a multistage pusher, cake buckling is reduced, as it may be a problem for a long, single-stage pusher. Because the cake thickness in each stage can be smaller (cake thickness is proportional to the basket length), a thinner cake results in more effective washing and dewatering. In addition, there is no cake heel, as the cake tumbles in transition from one stage to the next. This also helps to eliminate moisture retained by capillary rise in an otherwise undisturbed cake. Effective cake washing takes place at the transition between stages. Despite these advantages for the multistage, the single-stage can handle better bulk filtration than a multistage, in which it has to be accomplished in the first stage where length is limited. Because a thicker cake is formed on a one-stage basket, solids recovery is higher for the single-stage than for the multistage pusher. With either design, it is important that the cake thickness be circumferentially and axially uniform, with no axial ridges and valleys on the cake surface, which otherwise result in poor washing and dewatering.

Pusher centrifuges are used for dewatering and washing crystals and other particulate solids, including short fibers. The crystals in the feed should be 100 mesh (149 μm) or larger for good operation and to minimize loss of fine solids to filtrate. Feed-slurry concentration should be 35 percent by weight for conventional pushers. Lower concentrations can be tolerated on the cone-screen and multistage types, and especially the ones with better feed accelerators, which can handle higher liquid filtration. Washing efficiency of pusher centrifuges can be excellent, frequently in excess of 95 percent displacement of mother-liquor impurities with a wash-crystal weight ratio of only 1:10. Pusher centrifuges range in size from 300 to 900 mm (12 to 36 in), 4300 to 1300 mm long. They are operated at 400 to 900*g*. The upper range corresponds to a smaller unit.

Theory of Centrifugal Filtration Theoretical predictions of the behavior of solid-liquid mixtures in a filtering centrifuge are more difficult compared to pressure and gravity filtration. The area of flow and driving force are both proportional to the radius, and the specific

resistance and porosity may also change markedly within the cake. Filtering centrifuges are nearly always selected by scale-up from lab tests on materials to be processed, such as using bucket centrifuges where a wide range of test conditions (cake thickness, time, and *G*-force) can be controlled. Although tests with the bucket centrifuge provide some quantitative data to scale-up, the results include wall effect from buckets, which are not representative of actual cylindrical basket geometry. A modified version of the buckets or even a cylindrical perforated basket can be used. In the latter, there is less control of cake depth and circumferential uniformity. The desired quantities to measure are filtration rate, washing rate, spinning time, and residual moisture. Also, with filtering centrifuges such as the screen-bowl centrifuge, screen-scroll centrifuge, and to some extent in multistage pushers, the cake is constantly disturbed by the scroll conveyor or conveyance mechanism; liquid saturation due to capillary rise as measured in bucket tests is absent.

Filtration Rate When the centrifuge cake is submerged in a pool of liquid (Fig. 18-139*b*), as in the case of a fast-sedimenting, solids-forming cake almost instantly, and the rate of filtration becomes limiting, the bulk filtration rate Q for a basket with axial length b is:

$$Q = \frac{\pi b \rho K \Omega^2 (r_b^2 - r_p^2)}{\mu \left(\ln \left[\frac{r_b}{r_c} \right] + \frac{K R_m}{r_b} \right)} \qquad (18\text{-}116a)$$

where μ and ρ are, respectively, the viscosity and density of the liquid; Ω is the angular speed; K is the average permeability of the cake and is related to the specific resistance α by the relationship $\alpha K \rho_s = 1$, with ρ_s being the solids density; r_p, r_c, and r_b are, respectively, the radius of the liquid pool surface, the cake surface, and the filter medium adjacent to the perforated bowl. Here, the pressure drop across the filter medium, which also includes that from the cake heel, is $\Delta p_m = \mu R_m (Q/A)$ with R_m being the combined resistance. The permeability K has a unit m^2, α m/kg, and R_m m^{-1}. The driving force is due to the hydrostatic pressure difference across the bowl wall and the pool surface—i.e., the numerator of Eq. (18-116*a*), and the resistance is due to the cake layer and the filter medium—i.e., denominator of Eq. (18-116*a*). Fig. 18-150 shows the pressure distribution in the cake and the liquid layer above. The pressure (gauge) rises from zero to a maximum at the cake surface; thereafter, it drops monotonically within the cake in overcoming resistance to flow. There is a further pressure drop across the filter medium, the magnitude dependent on the combined resistance of the medium and the heel at a given flow rate. This scenario holds, in general, for incompressible as well as for compressible cake. For the latter, the pressure distribution also depends on the compressibility of the cake.

For incompressible cake, the pressure distribution and the rate depend on the resistance of the filter medium and the permeability of the cake. Figure 18-150 shows several possible pressure profiles in the cake with increasing filtration rates through the cake. It is assumed that $r_c/r_b = 0.8$ and $r_p/r_b = 0.6$. The pressure at $r = r_b$ corresponds to pressure drop across the filter medium Δp_m with the ambient pressure taken to be zero. The filtration rate as well as the pressure distribution depend on the medium resistance and that of the cake. High medium resistance or blinding of the medium results in greater penalty on filtration rate.

In most filtering centrifuges, especially the continuous-feed ones, the liquid pool above the cake surface should be minimum to avoid liquid running over the cake. Setting $r_p = r_c$ in Eq. 18-116*a*, the dimensionless filtration flux is plotted in Fig. 18-151 against r_c/r_b for different ratios of filter-medium resistance to cake resistance, KR_m/r_b. For negligible medium resistance, the flux is a monotonic decreasing function with increasing cake thickness, i.e., smaller r_c. With finite medium resistance, the flux curve for a range of different cake thicknesses has a maximum. This is because for thin cake the driving liquid head is small and the medium resistance plays a dominating role, resulting in lower flux. For very thick cake, despite the increased driving liquid head, the resistance of the cake becomes dominant; therefore, the flux decreases again. The medium resistance to cake resistance should be small, with $KR_m/r_b < 5$ percent (see Fig. 18-152). However, the cake thickness, which is directly proportional to the throughput, should not be too small, despite the fact that the machine may have to operate at somewhat less than the maximum flux condition.

It is known that the specific resistance for centrifuge cake, especially for compressible cake, is greater than that of the pressure or vacuum filter. Therefore, the specific resistance has to be measured from centrifuge tests for different cake thicknesses so as to scale up accurately for centrifuge performance. It cannot be extrapolated from pressure and vacuum filtration data. For cake thickness that is much smaller compared to the basket radius, Eq. (18-116*a*) can be approximated by

$$V_f = V_{fo} \left(\frac{h}{h_c} \right) \qquad (18\text{-}116b)$$

where $h = r_b - r_p$ is the liquid depth, $h_c = r_b - r_c$ is the cake thickness, and $v_{fo} = (\rho G K/\mu)$ is a characteristic filtration velocity. Table 18-14 shows some common filtering centrifuges and the application with respect to the *G*-level, minimum feed-solids concentration, minimum mean particle size, and typical filtration velocity. The vibratory and tumbler centrifuges have the largest filtration rate of 5×10^{-4} m/s (0.02 in/s) for processing 200-μm or larger particles, whereas the pen-

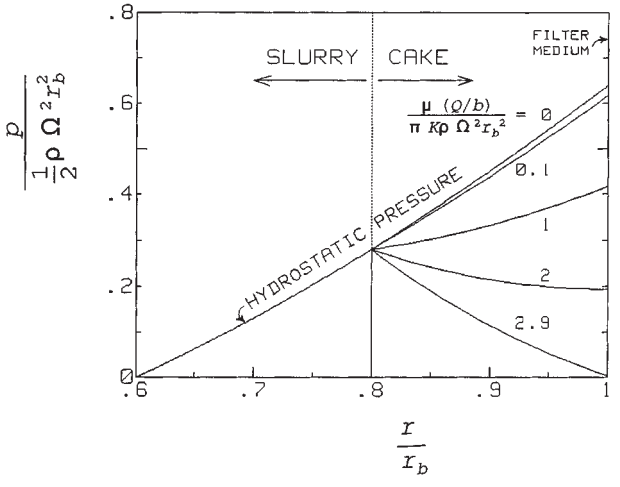


FIG. 18-150 Pressure distribution in a basket centrifuge under bulk filtration.

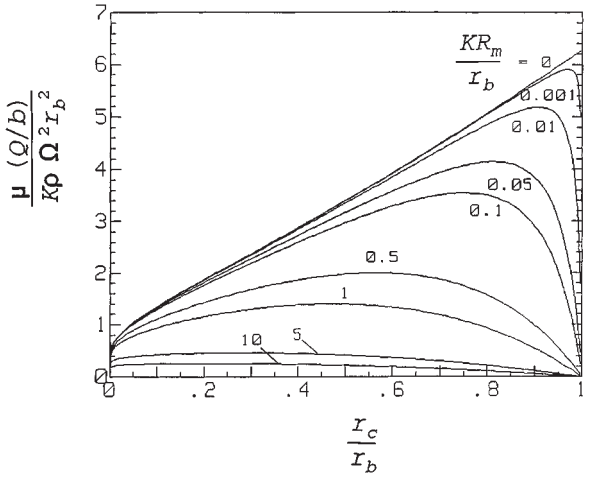


FIG. 18-151 Centrifugal filtration rate as a function of both cake and medium resistance.

dulum has the lowest filtration rate of 1×10^{-7} m/s (4×10^{-6} in/s) for processing 5-μm particles with increased cycle time. The screen-scroll, pusher, screen-bowl, and peeler centrifuges are in between.

Film Drainage and Residual Moisture Content Desaturation of the liquid cake ($S < 1$) begins as the bulk filtration ends, at which point the liquid level starts to recede below the cake surface. Liquids are trapped in: (1) cake pores between particles that can be drained with time (free liquid), (2) particle contact points (pendular liquid), (3) fine pores forming continuous capillaries (capillary rise), (4) particle pores or they are bound by particles (bound liquid). Numbers (1) to (3) can be removed by centrifugation, and, as such, each of these components depends on G to a different extent. Only desaturation of the free liquid, and to a much lesser entent the liquid at contact points, is a function of time. The wet cake starts from a state of being fully saturated, $S = 1$, to a point where $S < 1$, depending on the dewatering time. At a very large amount of time, it approaches an equilibrium point S_∞, which is a function of G, capillary force, and the amount of bound liquid trapped inside or externally attached to the particles.

The following equations, which have been tested in centrifugal dewatering of granular solids, prove useful:

Total saturation:

$$S_{\text{total}} = S_\infty + S_T(t) \tag{18-117}$$

Equilibrium component:

$$S_\infty = S_c + (1 - S_c)\,(S_p + S_z) \tag{18-118}$$

Transient component:

$$S_T(t) = (1 - S_c)\,(1 - S_p - S_z)S_t(t) \tag{18-119}$$

The details of the mathematical model of these four components are given below.

Drainage of free liquid in thin film:

$$S_t(t) = \left(\frac{4}{3}\right)\left(\frac{1}{t_d^n}\right), \quad t_d > 0 \tag{18-120}$$

where for smooth-surface particles, $n = 0.5$, and for particles with rough surfaces, n can be as low as 0.25.

Bound liquid saturation:

$$S_p = \text{function(particle characteristics)} \tag{18-121}$$

Pendular saturation:

$$S_z = 0.075, \quad N_c \le 5 \tag{18-122a}$$

$$S_z = \frac{5}{(40 + 6N_c)}, \quad 5 \le N_c \le 10 \tag{18-122b}$$

$$S = \frac{0.5}{N_c}, \quad N_c \ge 10 \tag{18-122c}$$

Frequently when $N_c < 10$, S_p and S_z are combined for convenience, the sum of which is typically 0.075 for smooth particles and can be as high as 0.35 for rough-surface particles. This has to be determined from tests.

Saturation due to capillary rise:

$$S_c = \frac{4}{B_o} \tag{18-123}$$

where the dimensionless time t_d, capillary number N_c, and Bond number B_o are, respectively:

$$t_d = \frac{\rho\, G d_h^2 t}{\mu\, H} \tag{18-124}$$

$$N_c = \frac{\rho\, G d_h^2}{\sigma \cos\theta} \tag{18-125}$$

$$B_o = \frac{\rho\, G H d_h}{\sigma \cos\theta} \tag{18-126}$$

where ρ and μ are, respectively, the density and viscosity of the liquid; θ is the wetting angle of the liquid on the solid particles; σ is the interfacial tension; H is the cake height; d is the mean particle size; and t is the dewatering time. The hydraulic diameter of the particles can be approximated by either $d_h = 0.667\,\varepsilon d/(1 - \varepsilon)$ or $d_h = 7.2(1 - \varepsilon)K^{1/2}/\varepsilon^{3/2}$, where ε is the cake porosity.

Example

Given: $\rho = 1000$ kg/m^3, $\rho_s = 1200$ kg/m^3, $\mu = 0.004$ N·s/m^2, $\sigma \cos\theta = 0.068$ N/m, $H = 0.0254$ m, $d = 0.0001$ m, $\varepsilon = 0.4$, $G/g = 2000$, $t = 2$ s, $S_p = 0.03$.

Calculate: $d_h = 4.4 \times 10^{-5}$ m, $t_d = 748$, $N_c = 0.56$, $B_o = 322$, $S_t = 0.048$, $S_z = 0.075$, $S_c = 0.012$, $S_\infty = 0.116$, $S_T = 0.043$, $S_{\text{total}} = 0.158$, $W = 0.919$.

Note that W is the solids fraction by weight and is determined indirectly from Eq. (18-86). The moisture weight fraction is 0.081.

The transient component depends not only on G, cake height, and cake properties, but also on dewatering time, which ties to solids throughput for a continuous centrifuge and cycle time for batch centrifuge. If the throughput is too high or the dewatering cycle is too short, the liquid saturation can be high and becomes limiting. Given that time is not the limiting factor, dewatering of the liquid lens at particle contact points requires a much higher G-force. The residual saturation depends on the G-force to the capillary force, as measured by N_c, the maximum of which is about 7.5%, which is quite significant. If the cake is not disturbed (scrolled and tumbled) during conveyance and dewatering, liquid can be further trapped in fine capillaries due to liquid rise, the amount of which is a function of B_o, which weighs the G-force to the capillary force. This amount of liquid saturation is usually smaller as compared to capillary force associated with liquid-lens (also known as pendular) saturation. Lastly, liquid can be trapped by chemical force at the particle surface or physical capillary or interfacial force in the pores within the particles. Because the required desaturating force is extremely high, this portion of moisture cannot be removed by mechanical centrifugation. Fortunately, for most applications it is a small percentage, if it exists.

SELECTION OF CENTRIFUGES

Table 18-15 summarizes the several types of commercial centrifuges, their manner of liquid and solids discharge, their unloading speed, and their relative volumetric capacity. When either the liquid or the solids discharge is not continuous, the operation is said to be cyclic. Cyclic or batch centrifuges are often used in continuous processes by providing appropriate upstream and downstream surge capacity.

Sedimenting Centrifuges These centrifuges frequently are selected on the basis of tests on tubular, disk, or helical-conveyor centrifuges of small size. The centrifuge should be of a configuration similar to that of the commercial centrifuge it is proposed to be used for. The results in terms of capacity for a given performance (effluent clarity and solids concentration) may be scaled up by using the sigma concept of Eqs. (18-114) to (18-116). Spin-tube tests may be used for information on systems containing well-dispersed solids. Such tests are totally unreliable on systems containing a dispersed phase that agglomerates or flocculates during the time of centrifugation.

Filtering Centrifuges These filters often can be selected on the basis of batch tests on a laboratory unit, preferably one at least 12 in (305 mm) in diameter. A bucket centrifuge test would be helpful to study the effect of G, cake height, and dewatering time. Caution has to be taken in correcting for capillary saturation, which may be absent in large continuous centrifuges with scrolling conveyances.

Unless operating data on similar material are available from other sources, continuous centrifuges should be selected and sized only after tests on a centrifuge of identical configuration.

It seems needless to state but is frequently overlooked that test results are valid only to the extent that the slurry and the test conditions duplicate what will exist in the operating plant. This may involve testing on a small scale (or even on a large one) with a slipstream from an existing unit, but the dependability of the data is often worth the extra effort involved. Most centrifuge manufacturers provide testing services and demonstration facilities in their own plants and maintain a supply of equipment for field-testing in the customer's plant, such as with a pilot centrifuge mounted on a mobile truck or trailer.

TABLE 18-15 Characteristics of Commercial Centrifuges

Method of separation	Rotor type	Centrifuge type	Manner of liquid discharge	Manner of solids discharge or removal	Centrifuge speed for solids discharge	Capacity*
Sedimentation	Batch	Ultracentrifuge				1 mL
		Laboratory, clinical	Batch	Batch manual	Zero	To 6 L
	Tubular	Supercentrifuge	Continuous†	Batch manual	Zero	To 1,200 gal/h
		Multipass clarifier	Continuous†	Batch manual	Zero	To 3,000 gal/h
	Disk	Solid wall	Continuous†	Batch manual	Zero	To 30,000 gal/h
		Light-phase skimmer	Continuous	Continuous for light-phase solids	Full	To 1,200 gal/h
		Peripheral nozzles	Continuous	Continuous	Full	To 24,000 gal/h
		Peripheral valves	Continuous	Intermittent	Full	To 3,000 gal/h
		Peripheral annulus	Continuous	Intermittent	Full	To 12,000 gal/h
	Solid bowl	Constant-speed horizontal	Continuous†	Cyclic	Full (usually)	To 60 ft^3
		Variable-speed vertical	Continuous†	Cyclic	Zero or reduced	To 16 ft^3
		Continuous decanter	Continuous	Continuous screw conveyor		To 54,000 gal/h
					Full	To 100 tons/h solids
Sedimentation and filtration		Screen-bowl decanter	Continuous	Continuous	Full	To 60,000 gal/h To 125 tons/h solids
Filtration	Conical screen	Wide-angle screen	Continuous	Continuous	Full	To 40 tons/h solids
		Differential conveyor	Continuous	Continuous	Full	To 80 tons/h solids
		Vibrating, oscillating, and tumbling screens	Continuous	Essentially continuous	Full	To 250 tons/h solids
		Reciprocating pusher	Continuous	Essentially continuous	Full	Limited data
	Cylindrical screen	Reciprocating pusher, single and multistage	Continuous	Essentially continuous	Full	To 50 tons/h solids
		Horizontal	Cyclic	Intermittent, automatic	Full (usually)	To 25 tons/h solids
		Vertical, underdriven	Cyclic	Intermittent, automatic, or manual	Zero or reduced	To 6 tons/h solids
		Vertical, suspended	Cyclic	Intermittent, automatic, or manual	Zero or reduced	To 10 tons/h solids

*To convert gallons per hour to liters per second, multiply by 0.00105; to convert tons per hour to kilograms per second, multiply by 0.253; and to convert cubic feet to cubic meters, multiply by 0.0283.

†Feed and liquid discharge interrupted while solids are unloaded.

COSTS

Neither the investment cost nor the operating cost of a centrifuge can be directly correlated with any single characteristic of a given type of centrifuge. The costs depend on the features of the centrifuge tailored toward the physical and chemical nature of the materials being separated, the degree and difficulty of separation, the flexibility and capability of the centrifuge and its auxiliary equipment, the environment in which the centrifuge is located, and many other nontechnical factors, including market competition. The cost figures presented herewith represent centrifuges only for use in the process industries as of 1996. In any particular installations, the costs may be somewhat less or much greater than those presented here.

The useful parameter for value analysis is the installed cost of the number of centrifuges required to produce the demanded separative effect (end product) at the specified capacity of the plant. The possible benefits of adjustments in the upstream and downstream components of the plant and the process should be carefully examined in order to minimize the total overall plant costs; the systems approach should be used.

Purchase Price Typical purchase prices, including drive motors, of tubular and disk sedimenting centrifuges are given in Table 18-16. The price will vary upward with the use of more exotic materials of construction, the need for explosion-proof electrical gear, the type of enclosure required for vapor containment, and the degree of portability, and this holds for all types of centrifuges.

The average purchase prices of continuous-feed, solid-bowl centrifuges made, respectively, of 316 stainless steel and steel are shown in Fig. 18-152. The average purchase prices of continuous-feed filtering centrifuges are shown in Fig. 18-153. This chart includes a comparison of prices on screen-bowl, pusher, screen-scroll, and oscillating conical baskets. On average, the screen bowl is approximately 10 percent higher in price than the solid bowl of the same diameter and length. This incremental cost results from the added complexity of the screen section, bowl configuration, and casing differences. Prices for both the solid-bowl and the filtering centrifuges do not include the drive motor,

TABLE 18-16 Typical Purchase Prices, Including Drive Motors, of Tubular and Disk Sedimenting Centrifuges, 1996

Type	Bowl diameter, in (mm)	Approximate Σ value, units of 10^4 ft^2 (10^3 m^2)	Designation	Purchase price, 1996 $
Tubular	4 (102)	2.7 (2.5)	Oil purifier	60,000–80,000
	4 (102)	2.7 (2.5)	Chemical separation	60,000–80,000
	5 (127)	4.2 (3.9)	Blood fractionation	100,000–140,000
Manual discharge disk	13.5 (343)	21 (20)	Hermetic	100,000–130,000
	24 (610)	95 (88)	Centripetal pump	150,000–300,000
Continuous nozzle-discharge disk	12 (305)	12 (11)	Clarifier	100,000–130,000
	18 (457)	25 (23)	Separator	150,000–200,000
	30 (762)	100 (93)	Recycle clarifier	270,000–300,000
Intermittent discharge disk	14 (356)	13 (12)	Centripetal pump	130,000–150,000
	18 (457)	22 (20)	Centripetal pump	170,000–200,000
	24 (610)	38 (35)	Centripetal pump	250,000–300,000

*NOTE: All prices quoted are for stainless steel construction with the exception of the oil purifier noted.

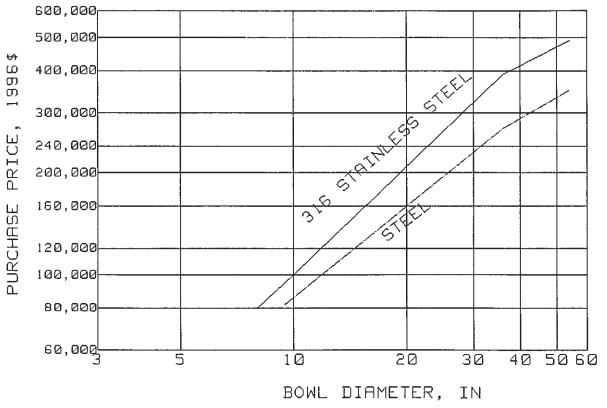


FIG. 18-152 Costs of continuous-feed solid-bowl.

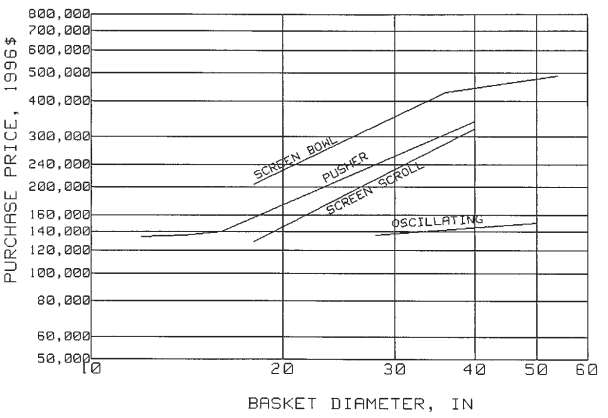


FIG. 18-153 Costs of continuous baskets (316 stainless steel).

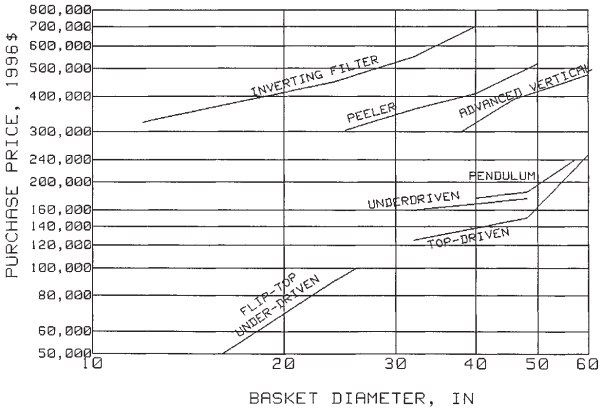


FIG. 18-154 Costs of batch baskets (316 stainless steel).

which typically adds another 5 to 25 percent to the cost. The higher end of this range represents a variable-speed-type drive. If a variable-speed backdrive is used instead of the gear unit, the incremental cost is about another 10 to 15 percent, depending on the capability.

The average prices of the batch centrifuge are shown in Fig. 18-154. All the models include the drive motor and control. In Fig. 18-154, the inverting filter, horizontal peeler, and the advanced vertical peeler are the premium baskets especially used for specialty chemicals and pharmaceuticals. Control versatility with the use of programmable logic control (PLC), automation, and cake-heel removal are the key features which are responsible for the higher price. The underdriven, top-driven, and pendulum baskets are less expensive with fewer features.

Installation Costs Installation costs of centrifuges vary over an extremely wide range, depending on the type of centrifuge, on the area and kind of structure in which it is installed, and on the details of installation. Some centrifuges, such as portable tubular and disk oil purifiers, are shipped as package units and require no foundation and a minimum of connecting piping and electrical wiring. Others, such as large batch automatic and continuous scroll-type centrifuges, may require substantial foundations and even building reinforcement, extensive interconnecting piping with required flexibility, auxiliary feed and discharge tanks and pumps and other facilities, and elaborate electrical and process-control equipment. Minimum installation costs, covering a simple foundation and minimum piping and wiring, are about 5 to 10 percent of purchase price for tubular and disk centrifuges; 10 to 25 percent for bottom drive, batch automatic, and continuous-scroll centrifuges; and up to 30 percent for top-suspended basket centrifuges. If the cost of all auxiliaries—special foundations, tanks, pumps, conveyors, electrical and control equipment, etc.—is included, the installation cost may well range from 1 to 3 times the purchase price of the centrifuge itself.

Maintenance Costs Because of the care with which centrifuges are designed and built, their maintenance costs are in line with those of other slower-speed separation equipment, averaging in the range of 5 to 10 percent per year of the purchase price for centrifuges in light to moderate duty. For centrifuges in severe service and on highly corrosive fluids, the maintenance cost may be several times this value. Maintenance costs are likely to vary from year to year, with lower costs for general maintenance and periodic large expenses for major overhaul. Centrifuges are subject to erosion from abrasive solids such as sand, minerals, and grits. When these solids are present in the feed, the centrifuge components are subject to wear. Feed and solids discharge ports, unloader knives, helical scroll blade tips, etc., should be protected with replaceable wear-resistant materials. Excessive out-of-balance forces strongly contribute to maintenance requirements and should be avoided.

Operating Labor Centrifuges run the gamut from completely manual control to fully automated operation. For the former, one operator can run several centrifuges, depending on their type and the application. Fully automatic centrifuges usually require little direct operation attention.

EXPRESSION

GENERAL REFERENCES: F. M. Tiller and N. B. Hsyung, "Compaction of Filter Cakes," *Advances in Filtration Separation Technology,* **5,** pp. 327–331 (1992). F. M. Tiller and C. S. Yeh, "Relative Liquid Removal in Filtration and Expression," *Filtr. Sep.,* **27,** p. 129 (1990). F. M. Tiller and C. S. Yeh, "The Role of Porosity in Filtration Part XI: Filtration Followed by Expression," *AIChE Journal,* **33**(8), p. 1241 (August 1987). F. M. Tiller, C. S. Yeh, and W. F. Leu, "Compressibility of Particulate Structures in Relation to Thickening, Filtration and Expression—A Review," *Separation Science and Technology,* **22**(2) and (3), pp. 1037–1063 (1987). Shirato, M. et al., "Deliquoring by Expression," in R. J. Wakeman (ed.), *Progress in Filtration,* **4,** Elsevier, pp. 181–287 (1986). M. Shirato et al., "Fundamental Studies on Continuous Extrusion Using a Screw Press," *International Chemical Engineering,* **18**(4), pp. 680–687 (October 1978).

DEFINITION

Expression, possibly followed by air (or steam) displacement, is the last stage in mechanically dewatering* compressible solids. Expression is used to wring out the last remaining liquid before resorting to thermal drying or solvent (chemical) extraction of the remaining liquids from the solids.† The goal of this stage of dewatering is maximum removal of liquid rather than creation of a solids-free liquid. The operating costs for expression are much lower than those for heat or solvent recovery, and the former is used in preference to the two latter processes. Tiller estimates that for pressures up to 1000 kPa (10 atm) the mechanical energy required for liquid removal is 400 times less than the thermal energy required for evaporation [Tiller, Yeh, and Leu, *Separation Science and Technology,* **22,** pp. 1037–1063 (1987)]. For sludges intended for incineration, expression can often dewater the material sufficiently to eliminate the need for auxiliary fuel. For example, in wastewater treatment plants, particularly those that include some form of thermal treatment, the degree of dewatering has a greater impact on the energy balance than any other single unit process [Campbell and Plaisier, *Advances in Filtration and Separation Technology,* **7** (System Approach to Separation and Filtration Process Equipment), pp. 583–586 (1993)].

APPLICATIONS

Typical materials that are or can be processed in various types of expression dewatering devices are listed in Table 18-17. The table also provides an indication of the efficiency of the equipment.

EQUIPMENT

In the past, expression presses were used in many processes for extracting oil and juice, generally from seeds and fruits such as olives. Batch presses were typically used in these applications, and hand unloading of the pressed cake was often required. Batch presses that require hand unloading or extensive cleaning between pressings are rarely used now; descriptions of various types are presented in earlier editions of this handbook. This section, therefore, describes mainly continuous presses.

Continuous is used here to include not only presses that take feed and produce dewatered product in a constant stream, but also automated batch presses that require little or no operator intervention during operating cycles. Continuous-expression presses, under this broader operational definition, include variable-volume filter presses (q.v.), which inflate a membrane against the cake to press additional liquid from the solids within the press; screw presses, which compress a generally fibrous or polymerized feed in a screw whose diameter increases as the feed progresses through the barrel; belt presses, which constrain the feed between two porous belts that are mechanically squeezed together; and rigid perforated disk or roll presses, which squeeze solids through a nip formed by converging rotating disks or in the nip between two parallel, closely spaced, porous drums. Many other types of presses are also available, but they are used less frequently. Among them is the tube press, which can exert higher overall pressure on filter cake than any other device. Although the tube press is technically a batch device like the variable-volume filter press, it can also be automated for continuous cycling.

Screw Presses Figures 18-155 and 18-156 show screw presses. The rotating screw shown in Fig. 18-156 is of constant pitch and has a constant diameter of about 0.3 m (12 in). Pressure to squeeze juice from fruit placed in the press comes from restricting the opening at the end of the barrel with a hydraulically adjustable cone and by making the spindle of the screw thicker toward the discharge end.

* Technically, the term should be *deliquoring* because this article concerns only separation of fluid from solids. However, in many applications the devices are intended for water removal, and *dewatering* is a common term. Therefore, the term *dewatering* will be used loosely in this article.

† Incompressible solids can be further mechanically dewatered by passing air or steam through a filter or centrifuge cake; for these materials, expression offers virtually no benefit.

The press in Fig. 18-156 is widely used in dewatering synthetic rubber crumb. With 200 to 250 connected horsepower, capacities range from 900 to 5000 kg/h (2000 to 11,000 lb/h) of solids. The hydraulic cylinders at the discharge end control the choke, or the space that the dewatered product must pass through to be discharged. The setting of the choke opening controls the dewatering that will be achieved, as well as the throughput. The approximate weight of the machine is 13.5 tonnes (15 tons). In other screw presses, the pitch of the screw can be tightened near the discharge end to apply higher pressures. The largest screw presses, used for sugar beets have 750-hp drives and weigh about 165 tonnes (185 tons). Processing capacity is 180,000 kg/h (400,000 lb/h). A few screw presses are built with a vertical shaft; these presses take up less floor space.

Disk Presses Figure 18-157 shows a disk press. The two disks, or press wheels, converge to a very narrow space at the bottom. This is the point of maximum compression, which can be more than 14 times the feed pressure. The press wheels have channels to carry the liquid from the dewatered product, and they are covered with a screen plate. Wheels 1.5 m (5 ft) in diameter are used on a large press that requires about 80 connected horsepower and produces just under 1 tonne/h (0.9 ton/h) of solids (dry basis). Typical applications are fibrous materials such as coffee grounds, pineapple and citrus peels and wastes, alfalfa, and brewer's spent grain.

Roll Presses The twin roll press shown in Fig. 18-158 is intended for paper pulp dewatering, specifically for one-step dewatering of an incoming slurry that starts at 2 to 5 percent solids and is dewatered to 50 percent. Other uses include citrus processing. The two rolls are perforated, and the mat to be dewatered forms on them. They rotate toward each other. Throughput and degree of dewatering depend on the size of the gap between the rolls, as well as on feed rate and solids consistency. The bottom vat is sealed so that the slurry can be pumped beneath the rolls under pressures up to 140 kPa (20 psig), and the rolls act as pressure filters until the cake is compressed between them as it is lifted out of the slurry by rotating the roll. The largest machines, with rolls 1.5 m (4.5 ft) in diameter and 7 m (21 ft) long, can produce up to 37 tonnes/h (41 tons/h), dry basis. Such machines weigh about 160 tonnes (180 tons) and require up to 450 connected horsepower.

Belt Presses Belt presses were fully described in the section on filtration. The description here is intended to cover only the parts and designs that apply expression pressure by a mechanism in addition to the normal compression obtained from tensioning the belts and pulling them over rollers of smaller and smaller diameters. The tension on the belt produces a squeezing pressure on the filter cake proportional to the diameter of the rollers. Normally, that static pressure is calculated as $P = 2T/D$, where P is the pressure (psi), T is the tension on the belts (lb/linear in), and D is the roller diameter. This calculation results in values about one-half as great as the measured values because it ignores pressure created by drive torque and some other forces [Laros, *Advances in Filtration and Separation Technology,* **7** (System Approach to Separation and Filtration Process Equipment), pp. 505–510 (1993)].

Expression belt presses (such as the Parkson Magnum Press) add an extra section to the path of the filter belts; an additional tensioned belt compresses the belts containing the filter cake to achieve a pressure of about 18 kg/cm (100 lb/linear in) instead of the pressure of 6 kg/cm (35 lb/linear in) achieved by a conventional dewatering belt press. Other expression dewatering belt presses, such as the Eimco Expressor Press shown in Figure 18-159, are designed with a large central drum and many smaller press rolls mounted radially around it. The smaller press rolls directly compress the two belts, and the filter cake enclosed between them is compressed against the larger perforated drum. This design can apply over 3500 kPa (500 psi), or 10 or more times as much pressure as that achieved by belt tensioning alone. Horsepower requirements are in the range of 10 to 40, and a large unit weighs about 11.5 tonnes (13 tons). A large press will process up to 13 tonnes/h (15 tons/h) of apples for juice extraction.

Variable-Volume Filter Presses These membrane filter presses are covered in the section on filtration. Two designs are used for the presses: (1) the typical variable-volume filter press has a normal vertical leaf design; (2) other presses, such as those provided by Filtra-Systems and Larox, are designed with horizontally arranged leaves.

TABLE 18-17 Materials Suitable for Dewatering in Expression Devices and Typical Performance

Type of press	Material	Feed	Product
Food and dairy products			
Oilseeds	Single screw		20% oil recovery
	Twin screw		94% oil recovery
Cocoa butter	Screw		
Alfalfa for silage	Screw	10–15	25–30
	Disk	10–15	25–35
Brewers' spent grain	Screw	20–25	30–35
	Disk	20–25	35–40
Corn silage	Screw		
Starch	Screw		
Citrus or pineapple peel, unlimed	Screw	15	20–25
	Disk	15	25–30
Citrus peel, limed for pectin	Screw	15	20–25
	Disk	15	25–30
Coffee grounds	Disk	20–25	45–50
Fish waste			
Sugar beets			
Sugarcane mud			
Spent tea	Expression belt	22	48
Fruit for juice	Expression belt	3	19
Slaughterhouse, tanning, and rendering waste and by-products			
Sewage sludge	Expression belt	4	36
Coagulated suspensions of rubber or polymers	Expression belt	48	90
		40–60	85–92
Pulp and paper mill sludges*	Expression belt	3	43
	Twin roll	3	35–50
	Screw	3	35
Fibrous materials (peat)*	Expression belt	18	35
	Variable-volume filter press	3	37
Fiberglass manufacturing scrubber sludge			
Secondary and synthetic fiber			
Chemicals			
Calcium carbonate	Expression belt	43	71
Calcium hypochlorite			
Calcium stearate			
Magnesium hydroxide	Expression belt	48	68
Biogums: xanthan, carrageenan	Screw	50–55	
Textile dyeing wastes	Screw	3	25–30
Paint and pigments	Expression belt	33	57
Ceramics, talc, and clay			
Paper and plastic fillers			
Metal ore concentrates	Variable-volume filter press	46–55	81–93*
Fine coal refuse			
Metal tailings			
Refinery sludges			
Wastewater treatment plant sludges			
Potable water treatment sludges			
Plating and other metal hydroxide sludges	Screw	5–6	30

*Final moisture content depends on operating conditions; longer cycles produce higher values.
*The results for these different presses are not directly comparable.
SOURCE: Various manufacturers.

Tube Presses The tube press (Denver Equipment Co.; Alfa-Dyne Div., Aquilla Eng.) achieves pressures of up to 13,800 kPa (2,000 psi). A tube with a central porous candle is sealed at the top, where the inlet for slurry is located, and at the space at the bottom between the tube shell and the porous candle. Feed is pumped into the annular space between the candle and inner wall of the tube, and clear liquid flows through the candle and out the bottom. When the pump is no longer capable of adding feed to the tube, the inlet is sealed, and a rubber bladder that lines the inside wall of the tube is expanded by pumping a fluid into the space between the tube and the rubber bladder. This forces the solids and the bladder against the central candle, completing the expression dewatering. After the bladder retracts, the bottom of the tube and the candle are dropped away from the tube to allow discharge of the dewatered, and usually quite hard, filter cake. Then the cycle starts again. Used on clays, calcium carbonate, mineral concentrates, and other inorganic solids, capacity ranges up to 1 tonne/h per tube.

OPTIMIZATION

The range of feed materials that are dewatered by expression devices is expanding, and the degree of dewatering achieved by each such devices is improving. Although new equipment design is responsible for most of the improvements, pretreatment of various feeds plays a critical role in allowing the expression presses to work on many feeds. Until recently, expression has been viewed as a brute force method; users generally ignored the properties of the feed. When feed materials would react to physical compression or shearing in the press by flowing, breaking down, or in some other way allowing the solids to follow the liquid out of the press, expression presses were not used.

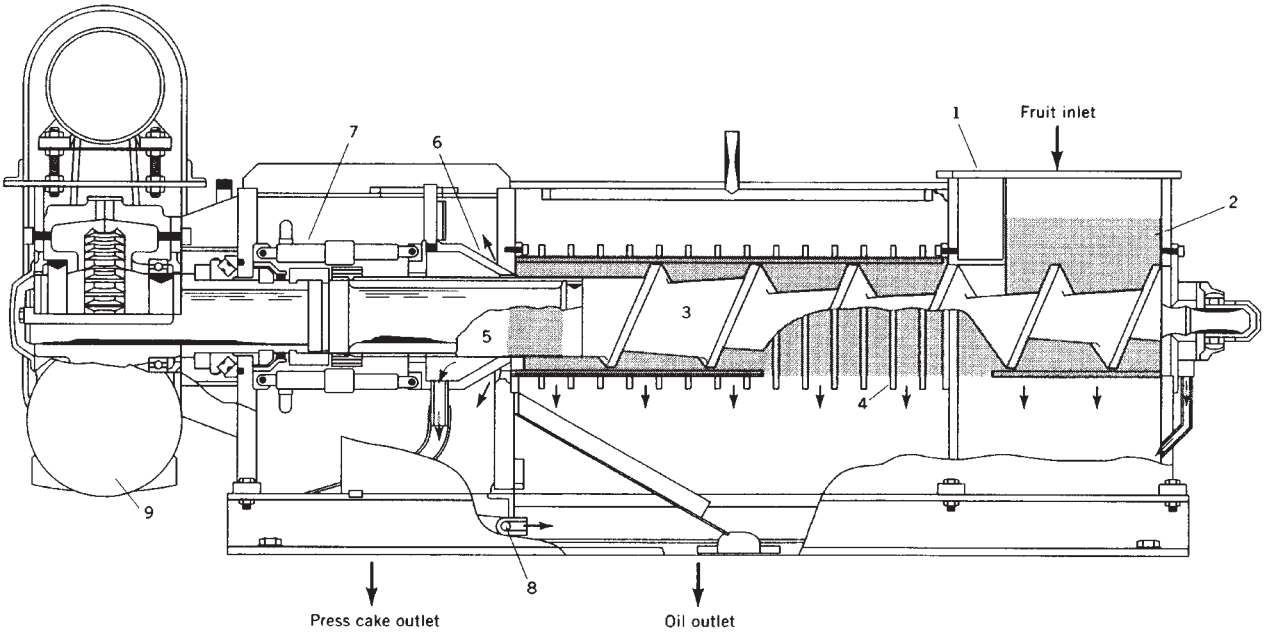


FIG. 18-155 Cross section of screw press used for fruit juice (32): (1) hopper, (2) perforated sheets, (3) main shaft, (4) perforated cage, (5) draining cylinder, (6) cone, (7) hydraulic cylinder, (8) draining cylinder oil, (9) gearbox. (*Courtesy of the French Oil Mill Machinery Co.*)

About the only treatment given to make a feed stay in the press while it was being dewatered was to add a **body feed.** The body feed would provide a network of pores and add some strength to the feed during the pressing cycle. Typical body feeds, used at 10 to 50 percent of the volume of the original dry solids content of the feed, include rice hulls, sawdust, bagasse, diatomaceous earth, kiln dust, flyash, or perlite. Fibrous body feeds are very effective in aiding screw-press performance. A recent trend is the addition of coagulants and synthetic flocculants. These additives make both screw and belt presses effective for dewatering sewage sludges and other fine-grained hydrophilic feeds.

In the past decade adjustments in many of the more subtle variables that affect the feed to a filter have begun to be used to control dewatering presses and improve their performance. These variables affect the permeability, compressibility, and rheological properties of the feed and the resulting cake. For example, pH, streaming potential,

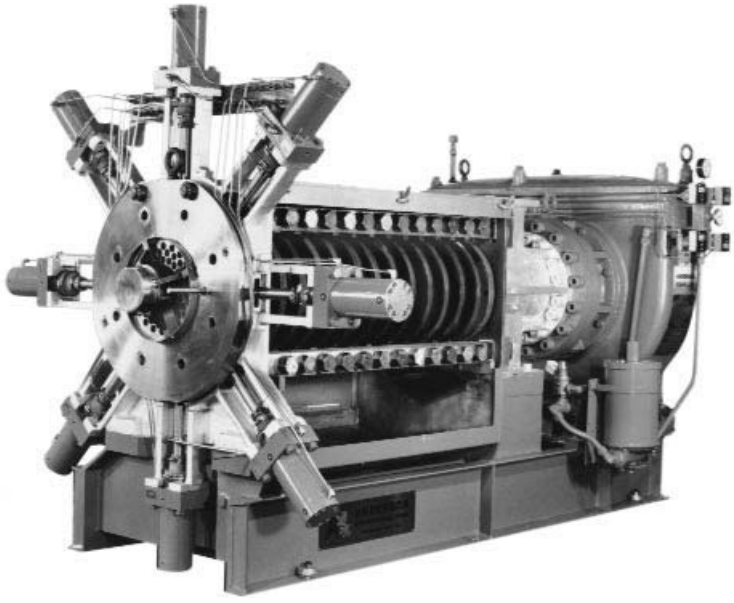


FIG. 18-156 Screw press. (*Anderson International Corp.*)

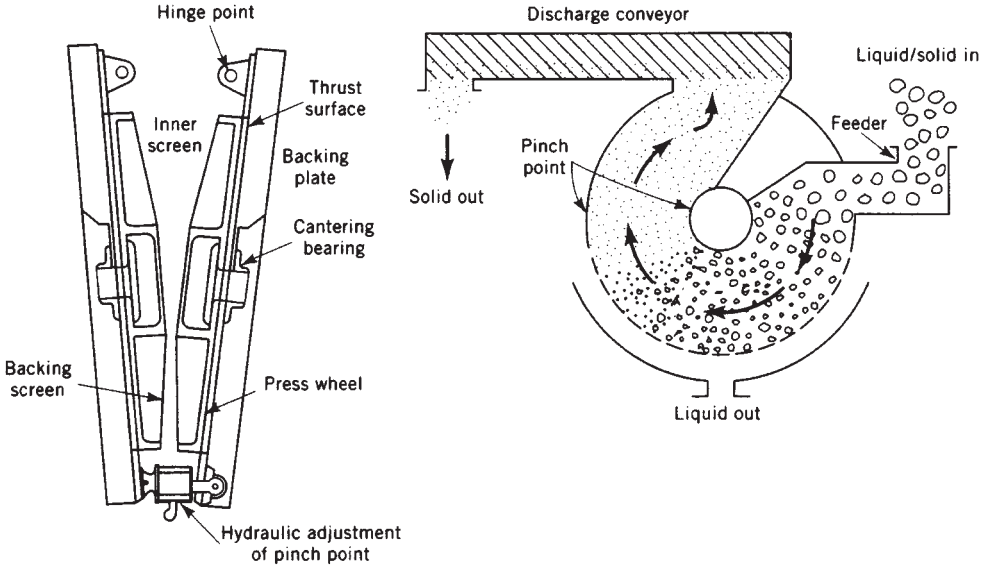


FIG. 18-157 Schematic of a disk press (41). (*Courtesy of Bepex Corp., a subsidiary of Berwind Corp.*)

viscosity, temperature, contact angle, and surface tension all affect filtration, and they can be adjusted to enhance expression dewatering as well. One indirect, continuous, online system controls polymer dosing by observing the reflectivity of the filter cake in the gravity drainage section of a belt filter press. Higher moisture content leads to high reflectivity, a condition that a human operator often uses to monitor performance [Ho, in B. M. Moudgil and B. J. Scheiner (eds.), "Flocculation and Dewatering," *Eng. Found. Conf.*, pp. 433–444 (Jan. 1988)]. Online control appears to be difficult to achieve [Campbell and Plaisier, *Advances in Filtration and Separation Technology*, **7** (System Approach to Separation and Filtration Process Equipment), pp. 583–586 (1993)].

Screw presses were traditionally used for seeds and fruits that had to be mechanically ruptured to release the liquid in the seeds or cells

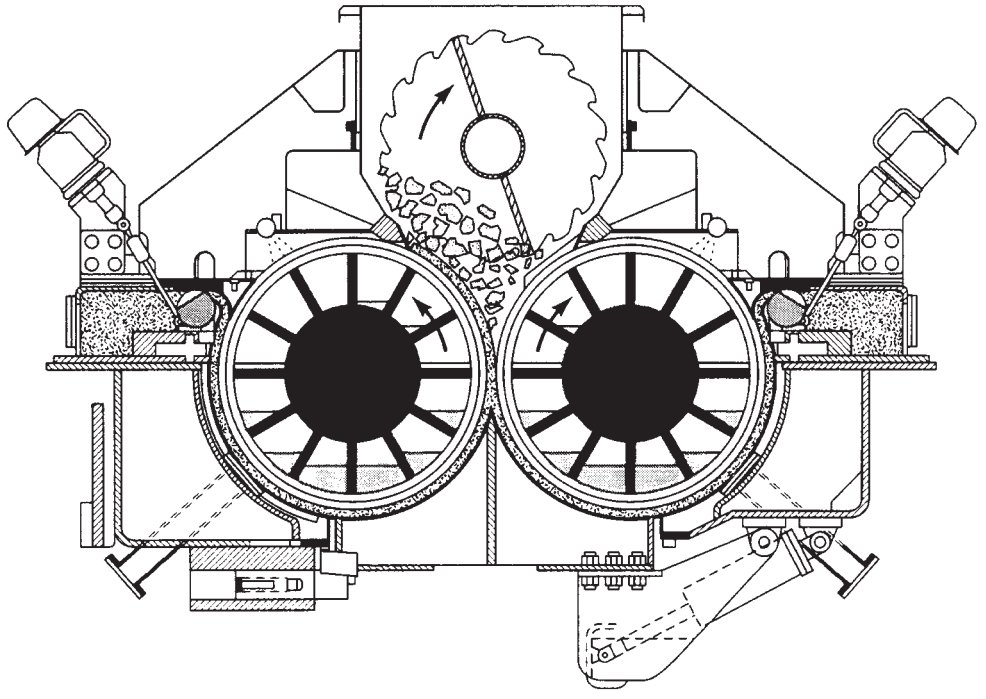


FIG. 18-158 Schematic of the Vari-Nip press (43). (*Courtesy of Ingersoll-Rand Co.*)

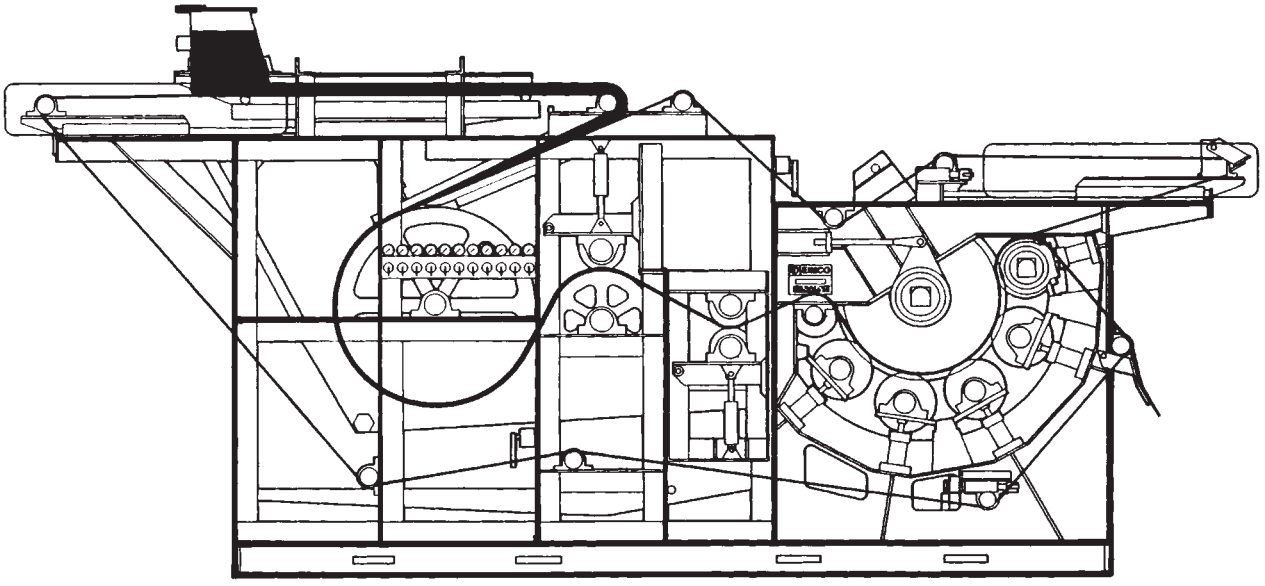


FIG. 18-159 Expressor press. (*Eimco Process Equipment Co.*)

of the fruit. Shearing was often required for effective rupturing of cells in those presses. However, when the feeds to the presses are agglomerated fine solids that are held together only by added flocculants and coagulants, shearing is not beneficial. Thus, designs of the presses for these two types of feeds have diverged. Designs for seeds emphasize shearing by placing screws nearly in contact with the perforated barrel or by using twin screws in a press. Designs for expressing without shearing emphasize the way the pitch and diameter in the screw press are varied in order to create squeezing with less shearing. Much less shearing occurs in a belt press, and still less occurs in an expression belt press. Variable-volume filter presses or tube presses give the least shearing for the most fragile cakes.

There is no substitute for fully testing various expression devices with specific feeds to determine their effectiveness. The only shortcuts are to seek the help of the press manufacturers and reagent suppliers in testing. Because performance of existing presses often depends critically on pretreatment of the feed, reagent suppliers are a good source for advice for improving continuing operations. For belt presses, small-scale test equipment can be used to predict the full-scale results of polymer selection and dosage [Novak, Knocke et al., *Water Sci. Technol.*, **28**(1), pp. 11–19 (1993); Kaesler, Connelly, and Richardson in B. M. Moudgil and B. J. Scheiner, op. cit., pp. 473–490].

THEORY

The variables affecting expression are known, can be described and modeled in a variety of ways, and are useful in understanding the principles of the mechanism of expression. They are not particularly useful in sizing operations or in choosing one type of press over another. The variables include those listed in Table 18-18.

The response of a cake to these properties is often not linear, and it can vary as conditions in the press change. This variability significantly complicates efforts to understand the process. For example, a highly compressible cake of latex in water easily dewaters with pressure, up to a point at which the latex particles deform and essentially create a barrier to further movement of water through the cake. Particle size and surface charge interact, but surface charge affects only small (<0.1-μm) particles. Not surprisingly, these interrelationships are described by empirical equations covering restrictive ranges.

TABLE 18-18 Variables Affecting Expression

Cake properties	Slurry feed properties	Equipment properties
Thickness	Liquid/solid ratio	Pressure
Specific cake resistance (porosity)	Viscosity	Homogeneity of cake as deposited on the filter medium
Compressibility, permeability	Temperature	Effect of mechanical forces on cake structure (e.g., shearing or axial loading)
Particle size, shape, degree of aggregation, and capillary pore size distribution	Surface tension, interfacial tension (contact angle)	Time the cake is subject to the highest pressures
Surface charge	pH, ionic concentration	Resistance to liquid flow through the filter medium and support
Size distribution	Rate of change in compressibility over time	Velocity required for the liquid to escape the expressed cake
Particle surface characteristics		
Type of solid (in terms of internal liquid content): gel, flocculated, hard particle		
Strength of particle (resistance to deformation under pressure)		

SELECTION OF A SOLIDS-LIQUID SEPARATOR

A good solids-liquid separator performs well in service, both initially and over time. It operates reliably day after day, with enough flexibility to accommodate to normal fluctuations in process conditions, and does not require frequent maintenance and repair. Selection of such a separator begins with a preliminary listing of a number of possible devices, which may solve the problem at hand, and usually ends with the purchase and installation of one or more commercially available machines of a specific type, size, and material of construction. Rarely is it worthwhile to develop a new kind of separator to fill a particular need.

In selecting a solids-liquid separator, it is important to keep in mind the capabilities and limitations of commercially available devices. Among the multiplicity of types on the market, many are designed for fairly specific applications, and unthinking attempts to apply them to other situations are likely to meet with failure. The danger is the more insidious because failure often is not of the clean no-go type; rather it is likely to be in the character of underproduction, subspecification product, or excessively costly operation—the kinds of limping failure that may be slowly detected and difficult to analyze for cause. In addition, it should be recognized that the performance of mechanical separators—more, perhaps, than most chemical-processing equipment—strongly depends on preceding steps in the process. A relatively minor upstream process change, one that might be inadvertent, can alter the optimal separator choice.

PRELIMINARY DEFINITION AND SELECTION

The steps in solving a solids-liquid separation problem, in general, are:

1. Define the overall problem, with expert assistance if necessary.
2. Establish process conditions.
3. Identify appropriate separator types; make preliminary selections.
4. Develop a test program.
5. Take representative samples.
6. Make simple tests.
7. Modify process conditions if necessary.
8. Consult equipment manufacturers.
9. Make final selection; obtain quotations.

Problem Definition Intelligent selection of a separator requires a careful and complete statement of the nature of the separation problem. Focusing narrowly on the specific problem, however, is not sufficient, especially if the separation is to be one of the steps in a new process. Instead, the problem must be defined as broadly as possible, beginning with the chemical reactor or other source of material to be separated and ending with the separated materials in their desired final form. In this way the influence of preceding and subsequent process steps on the separation step will be illuminated. Sometimes, of course, the new separator is proposed to replace an existing unit; the new separator must then fit into the current process and accept feed materials of more or less fixed characteristics. At other times the separator is only one item in a train of new equipment, all parts of which must work in harmony if the separator is to be effective.

Assistance in problem definition and in developing a test program should be sought from persons experienced in the field. If your organization has a consultant in separations of this kind, by all means make use of the expertise available. If not, it may be wise to employ an outside consultant, whose special knowledge and guidance can save time, money, and headaches. It is important to do this early; after the separation equipment has been installed, there is little a consultant can do to remedy the sometimes disastrous effects of a poor selection. Often it is best to work with established equipment manufacturers throughout the selection process, unless the problem is unusually sensitive or confidential. Their experience with problems similar to yours may be most helpful and avoid many false starts.

Preliminary Selections Assembling background information permits tentative selection of promising equipment and rules out clearly unsuitable types. If the material to be processed is a slurry or pumpable suspension of solids in a liquid, several methods of mechanical separation may be suitable, and these are classified into settling and filtration methods as shown in Fig. 18-160. If the material is a wet solid, removal of liquid by various methods of expression should be considered.

Settling does not give a complete separation: one product is a concentrated suspension and the other is a liquid which may contain fine particles of suspended solids. However, settling is often the best way to process very large volumes of a dilute suspension and remove most of the liquid. The concentrated suspension can then be filtered with smaller equipment than would be needed to filter the original dilute suspension, and the cloudy liquid can be clarified if necessary. Settlers can also be used for classifying particles by size or density, which is usually not possible with filtration.

Solid-liquid separation by screening is possible for some suspensions of coarse particles, but it is not widely applicable. For separation of fine solids from liquids, cake filtration or the newer systems for crossflow filtration should be considered. Crossflow filtration includes ultrafiltration, where the solids are very fine particles or macromolecules, and microfiltration, where the particle size generally ranges from 0.05 to 2 μm. In microfiltration, a suspension is passed at high velocity and moderate pressure (10 to 30 lb_f/in^2 gauge) parallel to a semipermeable membrane in sheet or tubular form. The solid particles are too large to enter the pores of the membrane and tend to accumulate at the membrane surface as the fluid passes through. However, high shear at the surface moves particles back into the fluid stream, and the solid is discharged as a concentrated suspension. This product suspension is similar to that produced in a settler, but the microfiltration equipment is much smaller for the same capacity. Also, by proper membrane selection, nearly clean liquid can be obtained as the permeate product.

SAMPLES AND TESTS

Once the initial choice of promising separator types is made, representative liquid-solid samples should be obtained for preliminary tests. At this point, a detailed test program should be developed, preferably with the advice of a specialist.

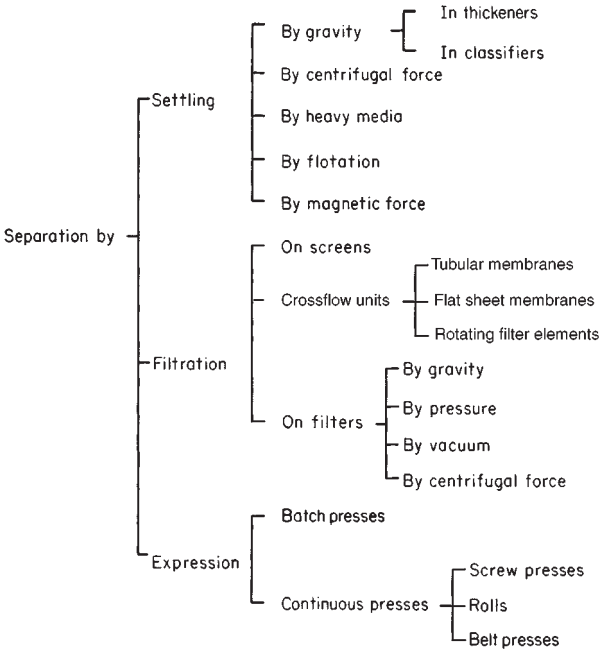


FIG. 18-160 Main paths to solids-liquid separation.

Establishing Process Conditions Step 2 is taken by defining the problem in detail. Properties of the materials to be separated, the quantities of feed and products required, the range of operating variables, and any restrictions on materials of construction must be accurately fixed, or reasonable assumptions must be made. Accurate data on the concentration of solids, the average particle size or size distribution, the solids and liquid densities, and the suspension viscosity should be obtained *before* selection is made, not after an installed separator fails to perform. The required quantity of the liquid and solid may also influence separator selection. If the solid is the valuable product and crystal size and appearance are important, separators that minimize particle breakage and permit nearly complete removal of fluid may be required. If the liquid is the more valuable product, can minor amounts of solid be tolerated, or must the liquid be sparkling clear? In some cases, partial or incomplete separation is acceptable and can be accomplished simply by settling or by crossflow filtration. Where clarity of the liquid is a key requirement, the liquid may have to be passed through a cartridge-type clarifying filter after most of the solid has been removed by the primary separator.

Table 18-19 lists the pertinent background information that should be assembled. It is typical of data requested by manufacturers when they are asked to recommend and quote on a solid-liquid separator. The more accurately and thoroughly these questions can be answered, the better the final choice is likely to be.

Representative Samples For meaningful results, tests must be run on representative samples. In liquid-solids systems good samples are hard to get. Frequently a liquid-solid mixture from a chemical process varies significantly from hour to hour, from batch to batch, or from week to week. A well-thought-out sampling program over a prolonged period, with samples spaced randomly and sufficiently far apart, under the most widely varying process conditions possible, should be formulated. Samples should be taken from all shifts in a continuous process and from many successive batches in a batch process. The influence of variations in raw materials on the separating characteristics should be investigated, as should the effect of reactor or crystallizer temperature, intensity of agitation, or other process variables.

Once samples are taken, they must be preserved unchanged until tested. Unfortunately, cooling or heating the samples or the addition of preservatives may markedly change the ease with which solids may be separated from the liquid. Sometimes they make the separation easier, sometimes harder; in either case, tests made on deteriorated samples give a false picture of the capabilities of separation equipment. Even shipping of the samples can have a significant effect. Often it is so difficult to preserve liquid-solids samples without deterioration that accurate results can be obtained only by incorporating a test separation unit directly in the process stream.

Simple Tests It is usually profitable, however, to make simple preliminary tests, recognizing that the results may require confirmation through subsequent large-scale studies.

Preliminary gravity settling tests are made in a large graduated cylinder in which a well-stirred sample of slurry is allowed to settle, the height of the interface between clear supernatant liquid and concentrated slurry being recorded as a function of settling time. Centrifugal settling tests are normally made in a bottle centrifuge in which the slurry sample is spun at various speeds for various periods of time, and the volume and consistency of the settled solids are noted. In gravity settling tests in particular, it is important to evaluate the effects of flocculating agents on settling rates.

Preliminary filtration tests may be made with a Büchner funnel or a small filter leaf, covered with canvas or other appropriate medium and connected to a vacuum system. Usually the suspension is poured carefully into the vacuum-connected funnel, whereas the leaf is immersed in a sample of the slurry and vacuum is applied to pull filtrate into a collecting flask. The time required to form each of several cakes in the range of 3 to 25 mm (⅛ to 1 in) thick under a given vacuum is noted, as is the volume of the collected filtrate. Properly conducted tests with a Büchner or a vacuum leaf closely simulate the action of rotary vacuum filters of the top- and bottom-feed variety, respectively, and may give the experienced observer enough information for complete specification of a plant-size filter. Alternatively, they may point to pressure-filter tests or, indeed, to a search for an alternative to filtration. Centrifugal

TABLE 18-19 Data for Selecting a Solids-Liquid Separator*

1. Process
   - *a.* Describe the process briefly. Make up a flowsheet showing places where liquid-solid separators are needed.
   - *b.* What are the objections to the present process?
   - *c.* Briefly, what results are expected of the separator?
   - *d.* Is the process batch or continuous?
   - *e.* Number the following objectives in order of importance in your problem: (*a*) separation of two different solids _____; (*b*) removal of solids to recover valuable liquor as overflow _____ ; (*c*) removal of solids to recover the solids as thickened underflow _____ or as "dry" cake _____; (*d*) washing of solids _____; (*e*) classification of solids _____; (*f*) clarification or "polishing" of liquid _____; (*g*) concentration of solids _____.
   - *f.* List the available power and current characteristics.

2. Feed
   - *a.* Quantity of feed:
     Continuous process: _____ gal/min; _____ h/day; _____ lb/h of dry solids.
     Batch process: volume of batch: _____ ; total batch cycle: _____ h.
   - *b.* Feed properties: temp. _____ ; pH _____ ; viscosity _____ .
   - *c.* What maximum feed temperature is allowable?
   - *d.* Chemical analysis and specific gravity of carrying liquid.
   - *e.* Chemical analysis and specific gravity of solids.
   - *f.* Percentage of solids in feed slurry.
   - *g.* Screen analysis of solids: wet _____ dry _____
   - *h.* Chemical analysis and concentration of solubles in feed.
   - *i.* Impurities: form and probable effect on separation.
   - *j.* Is there a volatile component in the feed? _____ Should the separator be vapor-tight? _____ Must it be under pressure? _____ If so, how much? _____

3. Filtration and settling rates
   - *a.* Filtration rate on Büchner funnel: _____ gal/(min)(ft²) of filter area under a vacuum of _____ in Hg. Time required to form a cake _____ in thick: _____ s.
   - *b.* At what rate do the solids settle by gravity?
   - *c.* What percentage of the total feed volume do the settled solids occupy after settling is complete? After how long?

4. Feed preparation
   - *a.* If the feed tends to foam, can antifoaming agents be used? If so, what type?
   - *b.* Can flocculating agents be used? If so, what agents?
   - *c.* Can a filter aid be used?
   - *d.* What are the process steps immediately preceding the separation? Can they be modified to make the separation easier?
   - *e.* Could another carrying liquid be used?

5. Washing
   - *a.* Is washing necessary?
   - *b.* What are the chemical analysis and specific gravity of wash liquid?
   - *c.* Purpose of wash liquid: to displace residual mother liquor or to dissolve soluble material from the solids?
   - *d.* Temperature of wash liquid.
   - *e.* Quantity of wash allowable, in lb/lb of solids.

6. Separated solids
   - *a.* What percentage of solids is desired in the cake or thickened underflow?
   - *b.* Is particle breakage important?
   - *c.* Amount of residual solubles allowable in solids.
   - *d.* What further processing will have to be carried out on the solids?

7. Separated liquids
   - *a* Clarity of liquor: what percentage of solids is permissible?
   - *b.* Must the filtrate and spent wash liquid be kept separate?
   - *c.* What further processing will be carried out on the filtrate and/or spent wash?

8. Materials of construction
   - *a.* What metals look most promising?
   - *b.* What metals must not be used?
   - *c.* What gasket and packing materials are suitable?

*U.S. customary engineering units have been retained in this data form. The following SI or modified-SI units might be used instead: centimeters = inches × 2.54; kilograms per kilogram = pounds per pound × 1.0; kilograms per hour = pounds per hour × 0.454; liters per minute = gallons per minute × 3.785; liters per second·square meter = gallons per minute·square foot × 0.679; and pascals = inches mercury × 3377.

filter tests are made in a perforated basket centrifugal 254 or 305 mm (10 or 12 in) in diameter lined with a suitable filter medium. Slurry is poured into the rotating basket until an appropriately thick cake—say, 25 mm (1 in)—is formed. Filtrate is recycled to the basket at such a rate that a thin layer of liquid is just visible on the surface of the cake. The discharge rate of the liquor under these conditions is the draining rate. The test is repeated with cakes of other thicknesses to establish the productive capacity of the centrifugal filter.

Batch tests of crossflow filtration can be carried out in small pressurized cells with a polymer, ceramic, or porous metal membrane at the bottom and a magnetic stirrer to provide high shear at the membrane surface. In other test cells, a pump circulates the suspension through a rectangular channel whose top or bottom surface is the selective membrane. Membranes with a wide range of permeabilities and pore sizes are available, and, to minimize plugging, the pore size is generally selected to be much smaller than the size of the particles in the suspension. The permeate flux (flow rate per unit area) is measured for different applied pressures and slurry concentrations, and the tests are continued for several hours to check for any flux decline caused by fouling of the membrane.

More detailed descriptions of small-scale sedimentation and filtration tests are presented in other parts of this section. Interpretation of the results and their conversion into preliminary estimates of such quantities as thickener size, centrifuge capacity, filter area, sludge density, cake dryness, and wash requirements also are discussed. Both the tests and the data treatment must be in experienced hands if error is to be avoided.

Modification of Process Conditions Relatively small changes in process conditions often markedly affect the performance of specific solids-liquid separators, making possible their application when initial test results indicated otherwise or vice versa. Flocculating agents are an example; many gravity settling operations are economically feasible only when flocculants are added to the process stream. Changes in precipitation or crystallization steps may greatly enhance or diminish filtration rates and hence filter capacity. Changes in the temperature of the process stream, the solute content, or the chemical nature of the suspending liquid also influence solids-settling rates. Occasionally it is desirable to add a heavy, finely divided solid to form a pseudo-liquid suspending medium in which the particles of the desired solid will rise to the surface. Attachment of air bubbles to solid particles in a flotation cell, using a suitable flotation agent, is another way of changing the relative densities of liquid and solid.

Consulting the Manufacturer Early in the selection campaign—certainly no later than the time at which the preliminary tests are completed—manufacturers of the more promising separators should be asked for assistance. Additional tests may be made at a manufacturer's test center; again a major problem is to obtain and preserve representative samples. As much process information as tolerable should be shared with the manufacturers to make full use of their experience with their particular equipment. Full-scale plant tests, although expensive, may well be justified before final selection is made. Such tests demonstrate operation on truly representative feed, show up long-term operating problems, and give valuable operating experience.

In summary, separator selection calls for clear problem definition, in broad terms; thorough cataloging of process information; and preliminary and tentative equipment selection, followed by refinement of the initial selections through tests on an increasingly larger scale. Reliability, flexibility of operation, and ease of maintenance should be weighed heavily in the final economic evaluation; rarely is purchase price, by itself, a governing factor in determining the suitability of a liquid-solids separator.

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Solid-Solid Operations and Equipment

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Most of the process industries deal with solid-solid systems which belong to the class of particulate systems. Particulate systems are composed of discrete solids known as particles dispersed in a gaseous or liquid phase. Solids dispersed in liquids are known as slurry systems. Thus, the processing of particulate solids might be carried out in either dry or wet state. Processing of particulate solids involves basically two kinds of operations: *mixing* leading to the generation of a homogeneous product, and *separation* in order to produce valuable solid components and to discard undesired less valuable solids.

The control of processes involving the treatment of solids generally requires means for careful sampling and analysis of solids and slurries at various points in an operation. Unlike liquids, particulate solids are not homogeneous. The composition of individual particles will vary with particle size and particle density. It follows that care must be exercised to take a sample that represents the entire solids mixture at the point of interest in the process. If the solids are not sampled in a representative manner, process and product control will not be reliable. The first subsection presents various aspects of sampling of solids and slurries including the underlying theory and details of different sampling equipment and their selection.

Mixing of solids is an important unit operation in the production of solids with consistent properties. A number of properties of the solid particles influence the mixing process, the design, and selection of mixing equipment. The second subsection elaborates on the theory of mixing, types of mixing equipment, and their operation.

Various techniques are available to separate the different types of particles that may be present in a solid mixture. The choice depends on the physicochemical nature of the solids and on site-specific considerations (for example, wet versus dry methods). A key consideration is the extent of the "liberation" of the individual particles to be separated. Particles attached to each other obviously cannot be separated by direct mechanical means except after the attachment has been broken. In ore processing, the mineral values are generally liberated by size reduction (see Sec. 20). Rarely is liberation complete at any one size, and a physical-separation flow sheet will incorporate a sequence of operations that often are designed first to reject as much

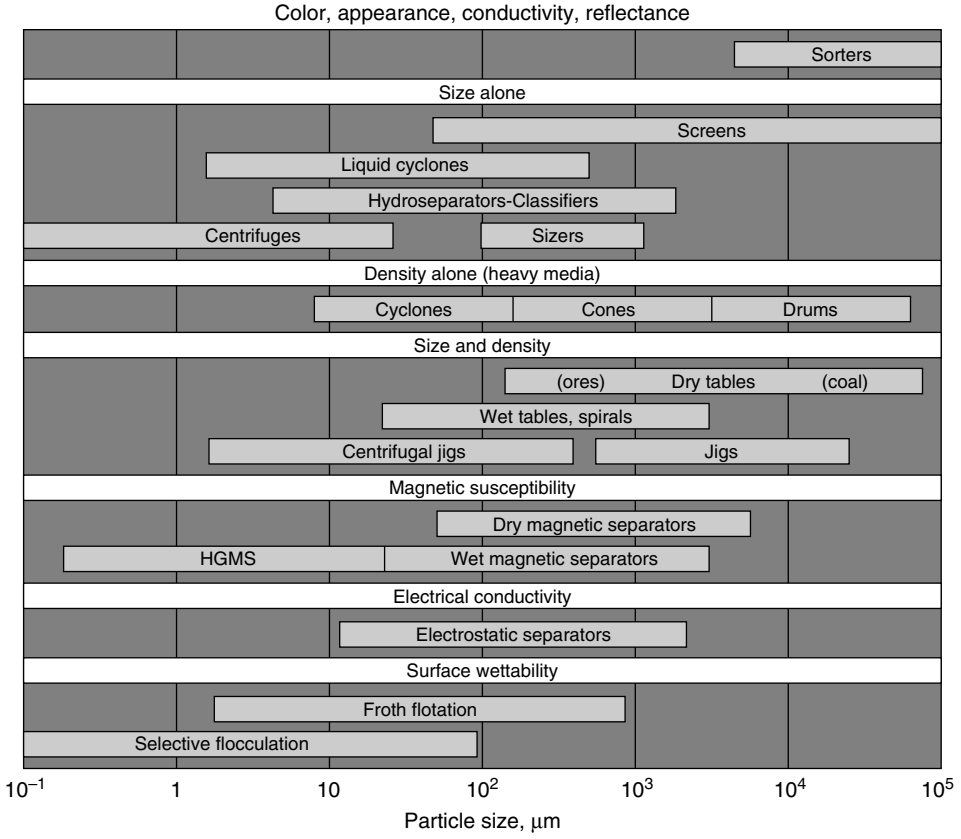


FIG. 19-1 Particle-size range as a guide to the range of applications of various solid-solid operations.

unwanted material as is possible at a coarse size and subsequently to recover the values after further size reduction.

Any difference in physical properties of the individual solids can be used as the basis for separation. Differences in density, size, shape, color, and electrical and magnetic properties are used in successful commercial separation processes. An important factor in determining the techniques that can be practically applied is the particle-size range of the mixture. A convenient guide to the application of different solid-solid separation techniques in relation to the particle-size range is presented in Fig. 19-1, which is a modification of an original illustration by Roberts et al.

The classification of solids by particle size is carried out for a number of reasons. Size classification can facilitate subsequent processing steps. An example is the scalping of tramp oversize material to avoid clogging a piece of processing apparatus. Similarly, better efficiency is achieved by removing fines before size reduction in crushers or ball or rod mills. Finished products generally are required to meet particle-size limits. Size separation is accomplished either in the dry condition or with the solids in suspension as a slurry. Wet classification allows higher process rates, particularly for materials of very fine sizes. Classification often is an integral part of a unit operation, as in closed-circuit grinding. Air classification methods for dry size classification in conjunction with size-reduction operations is covered in Sec. 20.

Gravity concentration is one of the oldest of the solids-separation techniques and the most important mineral-dressing method for obtaining ore concentrates. It is used mainly now for coal cleaning, yet Mills ["Process Design, Scale-Up and Plant Design for Gravity Concentration," in Mular and Bhappu (eds.), *Mineral Processing Plant Design,* 2d ed., Society of Mining Engineers, AIME, New York, 1980] notes that still more tonnage and greater values of material are concentrated by gravity methods than by a method such as froth flotation. The major unit operations which comprise gravity separation are jigging, tabling, spiral concentration, and dense-media separation. For high-capacity treatment of finer-sized low-grade ore materials, particularly the heavy mineral sands, the Reichert cone is becoming an industry standard [Ferree, "An Expanded Role in Minerals Processing Is Seen for the Reichert Cone," *Min. Eng.,* **25**(3), 29 (1973)].

Solids separation based on density loses its effectiveness as the particle size decreases. For particles below 100 microns, separation methods make use of differences in the magnetic susceptibility (magnetic separation), electrical conductivity (electrostatic separation), and in the surface wettability (flotation and selective flocculation). Treatment of ultrafine solids, say smaller than 10 microns can also be achieved by utilizing differences in dielectric and electrophoretic properties of the particles.

Physical separation methods are most widely used for the processing of coal and ore materials, and their basic development was designed for that purpose. Tremendous tonnages of solids are processed routinely at costs often as low at $1 per ton of material separated. The methods are applicable for other than ore processing, and solid-separation technology has become a more integral part of chemical-process operations. Recent requirements to recover values from various solid wastes have emphasized the need to adapt the relatively low-cost physical separation techniques of the ore processor, and as the needs to treat new types of materials and to improve recovery efficiency are constantly increasing, new designs are being developed.

The following subsections discuss the basic considerations involved in various unit operations of solid-solid separation and describe present industrial practice and equipment in general use.

SAMPLING OF DRY SOLIDS AND SLURRIES OF SOLIDS

References: Society of Mining Engineers, *Minerals Processing Handbook,* Norman L. Weiss, ed., chap. 30, "Sampling and Testing", part 2. "Theory and Practice of Incremental Sampling", Littleton, Colorado, 1985. Gy, Pierre M., *Sampling of Particulate Materials—Theory and Practice,* Elsevier Scientific Publishing Co., New York, 1979. Pitard, Francis F., *Pierre Gy's Sampling Theory and Sampling Practice,* CRC Press, Inc., Boca Raton, Florida, 1995. Gayle, G. B., *Theoretical Precision of Screen Analysis,* Report of Investigations No. 4993, U.S. Bureau of Mines, Dept. of Interior, Washington, D.C., 1952.

INTRODUCTION*

Sampling is a statistically derived process—a small amount of material S is taken from a large quantity B for the purpose of estimating properties of B. If S is an accurate sample (or stated more correctly, is representative of B according to a defined statistical parameter), it is a suitable estimator for the properties of B.

Sampling is typically required for quality control, wherein statistical data are compiled using specified procedures for mechanical sample collection and sample testing. Another sampling application is providing data for process control. A key factor in process-control sampling is minimizing time delays in making data available for use. Automatic analysis equipment is often employed, and the role of mechanical sampling becomes presenting samples for analysis by a reliable procedure.

The process of sample taking encompasses several steps, beginning with (1) taking a gross sample S from bulk materials B; (2) preparation of sample S for testing, which typically includes division of the sample and possible further substeps according to whether sampling is for analysis, size distribution, moisture, ash, and so on; and (3) the testing (analysis) step itself to determine properties of interest. Each step of the process contributes statistical error to the final result.

Estimations based on statistics can be made for total accuracy, precision, and reproducibility of results related to the sampling procedure being applied. Statistical error is expressed in terms of variance. Total sampling error is the sum of error variance from each step of the process. However, discussions herein will take into consideration only step (1)—mechanical extraction of samples. Mechanical-extraction accuracy is dependent on design reflecting mechanical and statistical factors in carrying out efficient and practical collection of representative samples S from a bulk quantity B.

Although mechanical sampling methods are to be the focus of attention, manual sampling methods are also employed for practical sample collection in commerce. Techniques of mechanical sampling should be emulated as closely as possible for best results with sampling by manual procedures.

Approved techniques for manual and mechanical sampling are often documented for various commodities handled in commerce by industry groups. Examples are the International Standards Organization (ISO), British Standards Association (BSA), Japan Institute of Standards (JIS), American Society for Testing Materials (ASTM), and the Fertilizer Institute. Sampling standards developed for use in specified industry applications frequently include instructions for laboratory work in sample preparation and analysis—steps (2) and (3) above.

Sampling techniques are more rigorous for materials with large variations in particle size and density compared to sampling of fine-sized powders. Coarse solids are often comprised of substantially differing mineral and crystalline forms within complex solids matrix. Fine-sized solid materials typically are relatively uniform in terms of chemical and physical characteristics with particle-size distributions and mineral densities usually within narrow ranges. Solids of organic chemical derivation and many commercial chemical materials, such as fertilizers, generally follow patterns of property distributions typical of powdered-mineral solids.

* Sampling of slurries and solids, differs fundamentally from sampling a completely mixed liquid or gas. A bulk quantity of solids incorporates characteristic heterogenity—that is, a sample S_1 differs inherently from a sample S_2 when both are taken from a thoroughly mixed load of solids as a result of property variances embodied in solids. In contrast, all individual samples from a completely mixed liquid or gas container are statistically identical.

The following discussion centers on sampling applications for powder solids comprised of small particulate sizes and equivalents in dry form or slurries. Sampling applications involving coarser solids (⅜ inch or 10 mm nominal size) as encountered in mineral products, typical ores, coal, and quarry rock for cement manufacture, are given more complete discussion in the *Mineral Processing Handbook* published by the Society of Mining Engineers and in other references (Pitard, Gy). "Nominal" particle size implies 95 percent through-screen particle size.

THEORY OF SAMPLING

Two principal topics are considered under theory of sampling. First is theory accounting for physical properties of material to be sampled. Second is the process of mechanical sample extraction. The theory predicts accuracy of sample taking—how much sample to take and how to take it to meet an accuracy specification.

Theory related to material characteristics states that a minimum quantity of sample is predicated as that amount required to achieve a specified limit of error in the sample-taking process. Theory of sampling in its application acknowledges sample preparation and testing as additional contributions to total error, but these error sources are placed outside consideration of sampling accuracy in theory of sample extraction.

Variations in measurable properties existing in the bulk material being sampled are the underlying basis for sampling theory. For samples that correctly lead to valid analysis results (of chemical composition, ash, or moisture as examples), a fundamental theory of sampling is applied. The fundamental theory as developed by Gy (see references) employs descriptive terms reflecting material properties to calculate a minimum quantity to achieve specified sampling error. Estimates of minimum quantity assumes completely mixed material. Each quantity of equal mass withdrawn provides equivalent representation of the bulk.

The theory enables a reasonable estimate of sample quantity needed to attain specified accuracy of a composition variable. The result is an ideal quantity—not realized in practice. Actual quantities for practical estimation are larger by an appropriate multiple to account for the reality that material is incompletely mixed when stored in stockpiles or carried on conveyors. Sample quantity to accommodate incompletely mixed solids can be specified through evaluating variance by autocorrelation of data derived with a series of stockpile samples, or from multiple sample extractions taken from a moving stream (Gy, Pitard).

In addition to composition factors, a sampling theory is available in sampling for size distribution. Quantity of sample needed to reach a specified error in determining size fraction retained on a designated screen is estimated by application of the binomial theorem (Gayle).

The second topic in theory of sampling pertains to mechanical sample taking. Design of mechanical sampling must conform to established criteria for sample-taking error to be minimal. This ensures error variance introduced by mechanical sample extraction is statistically insignificant compared to physical factors of sampling arising from heterogeneity, sample preparation, and sample testing sources of error.

Estimating Minimum Sample Quantity for Analysis The fundamental theory of sampling error variance can be applied to estimating a minimum quantity required from a completely mixed lot of solids for attaining an objective level of accuracy (Gy):

$$V = \left[\frac{1}{W_S} - \frac{1}{W_B}\right]\left[\frac{1-F}{F}\{(1-F)A_m + FA_g\}\right] fgbd^3$$

where V is the objective sampling-error variance (weight fraction), W_S is weight of the sample, W_B is weight of the bulk-solids lot, F is weight fraction mineral or other measurable quantity in the solids, A_m is density of mineral, and A_g is density of the nonmineral matrix.

Remaining terms to right of the bracket relate to properties to be measured within the matrix. The factor f is adjusted from 0 to 1 in relationship to the purpose of testing. A low value of f is indicated for scarce elements such as precious metals in electronic-source scrap. Moisture content has a high f value. The factor g is adjusted from 0 to 1 according to the degree of particulate classification. A high degree of size classification, as in a case of fine powders from screening, indicates values of 0.5 or higher. Unclassified fine solids from crushing have a value assigned to g of 0.25 or less. The factor b relates to size of elemental or crystal particles in bulk-solids particulate and degree of liberation ranging from 0 to 1. The term d is nominally the largest particle size. Estimated values employed in calculations rely on sampling experience and from solids-property investigation according to development of the theory, as described in related publications (Gy).

Example 1: Sample Quantity for Composition Quality Control Testing An example is sampling for quality control of a 1,000 metric ton (W_B) trainload of ⅜ in (9.4 mm) nominal top-size bentonite. The specification requires silica to be determined with an accuracy of plus or minus three percent for two standard errors (s.e.). With one s.e. of 1.5 percent, V is 0.000225 (one s.e. weight fraction of 0.015 squared). The problem to be solved is thus calculating weight of sample to determine silica with the specified error variance.

Bentonite has expected silica content of 0.5 weight percent (F is 0.005). Silica density (A_m) is 2.4 gm per cu cm, and bentonite (A_g) is 2.6. The calculation requires knowledge of mineral properties described by the factor ($fgbd^3$). Value of the factor can be established from fundamental data (Gy) or be derived from previous experience. In this example, data from testing a shipment of bentonite of 10 mesh top-size screen analysis determined value of the mineral factor to be 0.28. This value is scaled by the cube of diameter to ⅜-in screen size of the example shipment. The mineral factor is scaled from 0.28 to 52 by multiplying 0.28 with the ratio of cubed 9.4 mm (⅜-in screen top-size of the shipment to be tested) and cubed 1.65 mm (equivalent to 10 mesh).

Minimum weight W_S of sample is 110 kg from

$$0.000225 = \left[\frac{1}{W_S} - \frac{1}{10^6}\right]\left[\frac{1-0.005}{0.005}[(1-0.005)2.6 + (0.005)2.4]\right] 52$$

noting dimension of d^3 (particle diameter) is cubic mm requiring division by 1000 to rationalize with cubic cm of density. Sample weight in grams (from density) is divided by 1000 in converting to kg.

Estimating Change of Sampling Error with Change in Sample Size Increased accuracy in estimating a quality parameter by sampling through larger sample quantity can be estimated using the simplified Gy sampling equation

$$W_1V_1 = W_2V_2$$

W and V are values for sample weights and variances of parameter measurements at states 1 and 2 respectively.

Example 2: Calculation of Error with Doubled Sample Weight Repeated measurements from a lot of anhydrous alumina for loss on ignition established test standard error of 0.15 percent for sample weight of 500 grams, noting V is the square of s.e. Calculation of variance V and s.e. for a 1000 gram sample is

$$V = \frac{(0.15)^2(500)}{(1000)} = 0.01125;\ \text{standard error} = 0.11\ \text{percent}$$

Estimating Minimum Sample Quantity for Size Distribution Testing A simplistic approach to specifying minimum sample size for estimating particle distributions within allowed variance is based on a screening process in terms of binomial distribution. Each screening event is an outcome of two possibilities—particles either pass the screen or not. A relationship according to this principle presented by Gayle (loc. cit.) is employed in the example. Further development of sampling concepts for particle-size distribution is provided in the references (Pitard).

Example 3: Calculating Sample Weight for Screen-Size Measurement Weight W of bulk sample for screen analysis is calculated by the Gayle model for percent retained on a specified screen with relative standard error s.e. in percent

$$W = \frac{G(100-G)w}{V};\quad \text{example } W = \frac{5.5(100-5.5)0.0120}{1.56} = 4.0$$

where G is the weight percent of the sample retained on the given screen either as determined by testing or defined per specification, and w is the weight of a particle of the size retained on that screen.

Sample weight estimated in this example is for two standard errors of 2.5 percent (resulting in V of 1.56) for testing iron ore (hematite) retained on a ½-in screen. Estimate of G is 5.5 for 94.5 percent of weight passing. Particle weight

w retained on a ½-in opening screen assuming spherical shape and 5.1 specific gravity is 0.0120 lb. The calculation yields 4.0 lb as a minimum sample size, W.

Estimating Minimum Sample Quantity for Moisture Measurement Estimates of material quantity for testing moisture content depend on mechanisms of moisture distribution in the material. Moisture is physically retained on particle surfaces, chemically adsorbed on surfaces and within pores of particulate solids, and contained as an internal constituent of solids. Significant internal moisture is most often encountered in organic and agricultural source materials.

Sample quantity to estimate moisture for specific material is influenced to various levels of significance by properties such as particle-size range as well as relative amounts of moisture distributed among denoted forms of retention. Practical sample size estimates require background knowledge of parameters derived from experience for specific materials. More detailed examination of moisture-sampling aspects is provided in reference texts (Pitard).

Example 4: Calculation of Sample Weight for Surface Moisture Content An example is given with reference to material with minimal internal or pore-retained moisture such as mineral concentrates wherein physically adhering moisture is the sole consideration. With this simplification, a moisture coefficient K is employed as multiplier of nominal top-size particle size d taken to the third power to account for surface area. Adapting fundamental sampling theory to moisture sampling, variance is of a minimum sample quantity is expressed as

$$V = \left[\frac{1}{W_S}\right]\left[\frac{1-F}{F}\right]Kd^3; \text{ example } 0.0000562 = \frac{0.95\ 5\ 0.00633}{W_S\ 0.05\ 1728}$$

where V is variance in weight fraction, W_S is minimum weight of sample, F is nominal weight fraction moisture, and K is a constant with dimension mass per unit volume. In absence of prior knowledge for material surface moisture characteristics, a value of K equal to 5 lb/ft^3 can be used for typical mineral concentrates and other nonabsorbing fine materials. This relationship is applied in an example of a crystalline product—hydrated sodium sulfate (Glaubers salt) with d of minus 4 mesh (0.185 in). Standard material moisture content is 5 percent by weight, with required sampling error of 1.5 percent relative to total weight for two s.e. Variance for this value in weight fraction is 0.0000562 in calculating 6.1 lb as sample weight (1728 converts in^3 to ft^3).

MECHANICAL DELIMITATIONS OF SAMPLING

Sample increment extraction requires a cutter to move through (traverse) a flowing stream being sampled while meeting accepted criteria of design and operation. Two methods of mechanical sampling for materials in flow regime are employed. A preferred first method is sample extraction from material in gravity free fall, such as from trajectory discharge at the head pulley of a conveyor or gravity flow down an enclosed chute. Cutter motion can be linear or rotational with constant speed while taking samples by traversing a gravity free-fall flow stream.

Sampling is required to meet the principle of mechanical sample extraction in maintaining statistical validity. This principle states that the cutter must take through-stream extractions during each traverse of the flow stream being sampled such that each particle in the flow stream at any place in the stream has equal probability of being extracted into sample. The diagram of Fig. 19-2 illustrates a typical arrangement meeting criteria (sampling delimitations) for a linear-traversing cutter installation extracting from a free-fall stream of material.

An alternative method is sampling directly from a moving or stationary conveyor with cutter traverse through the complete material bed carried on the conveyor. The alternative method cannot assure executing complete extractions, or through-stream sampling, because in many applications residual fines from the material stream remain on the conveyor surface.

The alternative method of sample extraction is termed the *cross-stream* sampling method, or *cross-belt* when used in conjunction with a belt conveyor. Sample extraction typically take place with a belt conveyor in motion. However, with a rotary table-feeder conveyor, extractions are made with the table stopped. A cutter can perform extractions by this means from a machined flat surface with negligible

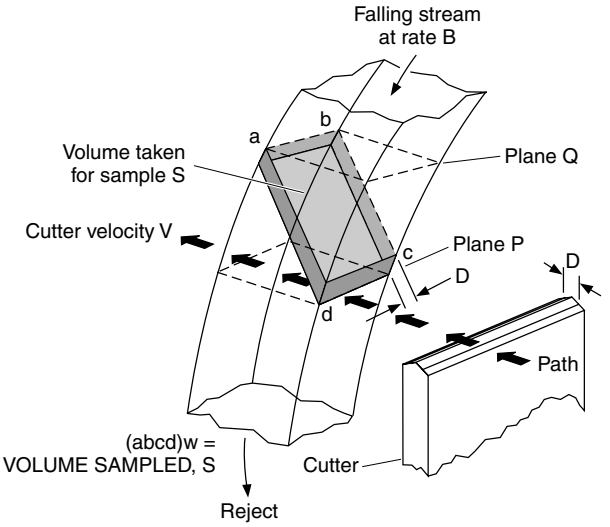


FIG. 19-2 Through-stream linear sampling. (*Courtesy of Harrison R. Cooper Systems, Inc. Salt Lake City, Utah.*)

residual fines left out of the sample. When sampling from a moving belt conveyor, residual fines become more significant resulting in loss of accuracy in extractions. This is due to clearances necessary between cutter edges and the conveyor belt, and also due to belt surface irregularities.

CRITERIA FOR SAMPLER DESIGN

Operation of a traversing sampler for *gravity flow* of material for through-stream sampling is required to meet the following design factors:

1. The cutter moves at constant speed (or constant rotation rate in the case of a rotary-motion sample cutter) such that the entire flow of material is traversed by the cutter, with the further requirement that the stopped position of the cutter at either limit of traverse (out of stream) is at sufficient distance from the stream so that no material from the stream enters the cutter while it is held stationary between traversing operations.
2. The sample cutter opening is set to specified width according to a multiple of the maximum (nominal) size of particulate being sampled and selected speed of the cutter. A minimum width of 10 mm or 0.375 in is recommended unless material is moist or has other properties to induce bridging of the cutter, suggesting need for a wider opening for practical operation. Experiments have determined that a cutter opening of a multiple of three times the nominal largest particle size and an 18-inches-per-second cutter speed (0.46 meters per second) is optimum to minimize sample extraction quantity with negligible delimitation error for fine-sized materials.
3. Cutter blade length extends beyond the material stream width on either side of the stream and volume of the cutter is sufficient to ensure all material taken into sample can be contained in the cutter body. Cutter blades are parallel, and are beveled to a sharp edge in the case of linear-motion traverse. For rotary-motion sample cutters, sharp edges of the cutter blades are radial to the center point of rotation.

Criteria for mechanical delimitations in sampling by the alternative cross-stream method to fulfill through-stream extraction requirements are revised from gravity-sampling criteria in the following respects:

1. The cutter opening is to exceed maximum (nominal) particle size by sufficient clearance to ensure that a large particle will not wedge into the opening. Sampling error due to free-fall deflection is avoided as a factor in setting cutter opening width. A 2 inch minimum cutter opening, required for practical operation, is recommended.

2. The cutter length should be approximately equal to the width of the material load carried on the conveyor.
3. When sampling from moving belt conveyors, the cutter operates in a radial mode with the belt surface contoured at the point of sampling by idlers, fixing radial curvature to the outer radius of the cutter. Clearance is minimized between outer edges of cutter blades and belt surface by cutter-shaft adjustment in the drive-clamping bracket.
4. Cutter speed at the outer radius is recommended at twice the conveyor belt speed for through-stream extractions from moving belts. The cutter is adjusted in a lateral angle to a 30-degree position, matching the cutter extraction path through the material bed on the belt at specified speed.

Cross-stream sampling from flat surfaces with material handled on a linear conveyor or rotary table is best carried out with the conveyor stopped. Sample extraction is then performed by linear traverse.

MECHANICAL SAMPLING EQUIPMENT

Repeating an axiom stated earlier, mechanical samplers are designed to extract increments of sample from a bulk quantity of material *B* in a manner that increments *S* are representative within statistical bounds of the bulk *B*. Further, the sampler is designed and constructed in conformance to criteria stated previously under "Mechanical Delimitations of Sampling" to assure that negligible errors arise from mechanical influence.

Many designs of equipment purported for sample extraction have been offered to industry or placed into service for sampling that fail to meet accepted mechanical standards. Extracted increments often have bias—inaccuracies found from tests on increments showing deviations usually with more or less fixed offset from true median values, or otherwise producing inconsistent and statistically poor test data compared to true values. Extraction increments using nonconforming designs may best be regarded as specimens of bulk *B*, but not samples in the statistical sense.

Mechanical sampling procedures further discussed are limited to sampling of flowing materials. Dry solid flows carried on a conveyor or in chute gravity fall are subject to through-stream sampling designed to extract correctly defined increments. Slurry gravity flows in launders and sloped pipes are sampled at the point of discharge, or slurries are sampled at open discharge from a vertical gravity pipe.

Static sampling methods with mechanical systems to operate thief-pipe sampling of solids taking increments from railroad hopper cars, trucks, or bins are seen in use. These are considered manual sampling methods operated mechanically. Applying criteria of through-stream sample extraction is infeasible, and it is inherently understood that bulk materials to be sampled in this manner are not perfectly mixed. An assured mode of sampling is providing through-stream sample extraction of bulk materials as they are loaded into bins, rail cars, trucks, and so on.

Various static thief or pipe samplers, often including pumps for stream transfers, are employed in slurry flows as well. These lack validity in terms of through-stream extraction capability. A pressure-thief sampler mounted on a pump discharge flange can be an approximation to through-stream sampling with assumption of complete mixing in flow from the pump if time lapse for flow to the thief from a pump is minimal, and pipe bends or other elements inducing classification are absent.

SELECTING A SAMPLER

Mechanical samplers meeting delimitation criteria are available in two basic designs for sampling material in gravity free fall. The basic designs are sampling with linear cutter motion and sampling with radial cutter motion (see Fig. 19-3 and Fig. 19-4 respectively). The net result is the same with either when equipment is properly designed and operated.

Selection of linear or radial (rotary cutter) sampling is made according to mechanical installation factors often on a basis of flow quantity. Smaller flows can be sampled in a cost-effective manner by rotary cutter samplers (frequently termed "vezin" design samplers, see Fig. 19-4).

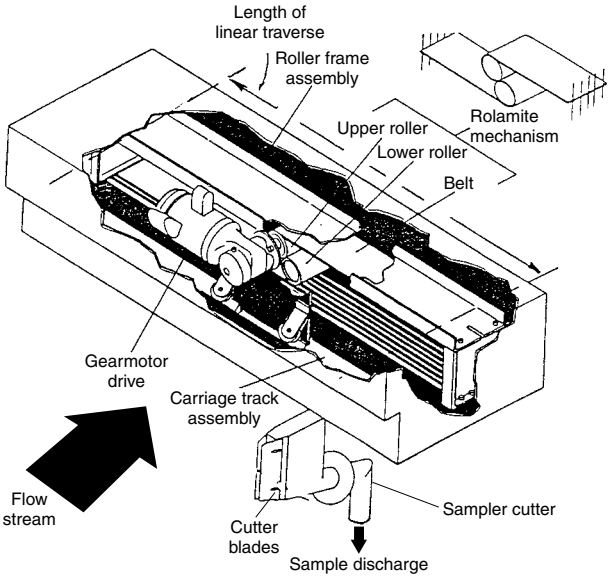


FIG. 19-3 Traversing sampler. (*Courtesy of Harrison R. Cooper Systems, Inc. Salt Lake City, Utah.*)

Sampling directly from material lying on the conveyor using a cross-stream cutter for extracting sample increments is diagrammed in Fig. 19-5 for moving conveyor belts and in Fig. 19-6 for a rotary table application. Cross-stream sampling can frequently be applied with acceptable delimitation error to materials of relatively low particle size and minimal variation, and also to materials with moisture content sufficient to avoid fines classification onto conveyor surfaces. A brush fixed to the cutter trailing edge aids in fines extraction to minimize residual sample remaining on the belt surface following cutter traverse.

In Fig. 19-5, the conveyor belt is radially profiled at the point of sample extraction with contouring idlers set to match the path of the cutter moving from its driveshaft rotation axis. Cutter edges are posi-

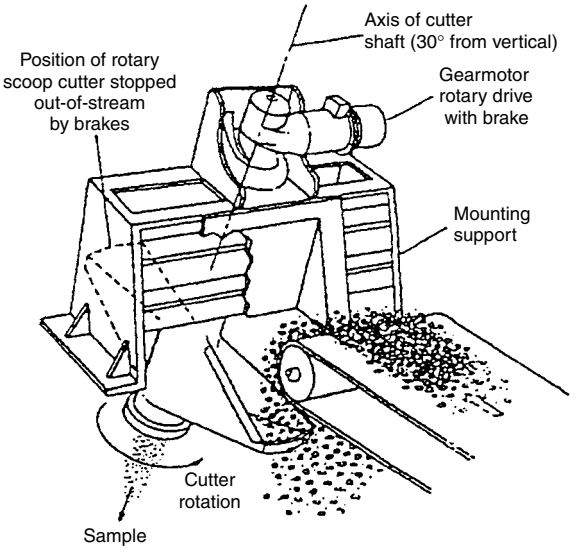


FIG. 19-4 Rotary sampler. (*Courtesy of Harrison R. Cooper Systems, Inc. Salt Lake City, Utah.*)

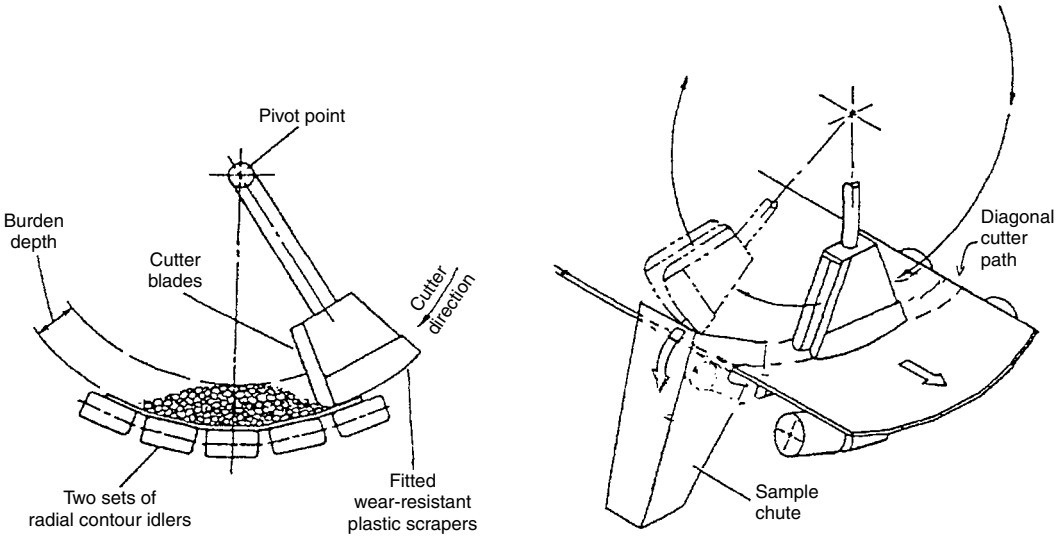


FIG. 19-5 Cross-belt sampler. (*Courtesy of Harrison R. Cooper Systems, Inc. Salt Lake City, Utah.*)

tioned with minimum clearance from the belt surface as is reasonably accomplished without contact of the cutter with the belt surface. Cutter blades are angled 30 degrees from the conveyor belt direction in positioning the cutter to its path through the conveyor belt load for cutter speed twice conveyor speed.

Extractions performed with the conveyor stopped allow more assured accuracy by the certainty of including fines in the sample increment. Sampler design to extract increments from a flat belt or rotary table sampler while the conveyor is stopped minimizes potential for residual fine particles remaining on the conveyor surface in carrying out extractions. See Fig. 19-6 for rotary table sampler extraction diagram.

Composite Samples Obtained by Multiple Sample Extractions Material flow streams are sampled in practice by combining extractions taken at successive time intervals into a composite sample. Multiple increment collection to obtain representative composite samples for specified bulk-material flows is performed according to a designated process in accommodating the presence of material property variations.

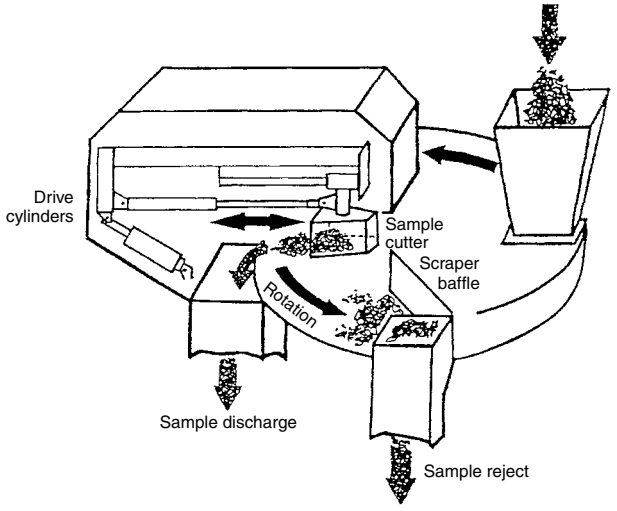


FIG. 19-6 Rotary-table sampler. (*Courtesy of Harrison R. Cooper Systems, Inc. Salt Lake City, Utah.*)

The requirement is to obtain proportional samples from the flowing material. This is accomplished in a technically accurate procedure by extractions taken on fixed time intervals. Variable time intervals with intervals determined from random selection are optionally employed to avoid bias error in sampling when characteristic periodic effects are known to be present in the stream of material. Possibilities for fixed sampling intervals to systematically coincide with periodicities are avoided by random time interval selection. Setting sampling intervals to material flow quantity, as in using belt weigh scale readings, opens potential for nonproportionalities and error in the composite sample.

Sampling of specified material flows to obtain representative composite quantities is a common practice for material accounting and quality control. A typical case is composite sampling of a shipload or trainload cargo transfer for either receiving or delivering materials. Another frequently used specification is eight-hour shift production quantities to be sampled to generate composite samples for testing.

Industry standards are frequently applicable in designing sampling procedures for many commodities in commerce transferred by ship cargoes or trainloads. Standards for iron ore, coal, metallurgical concentrates, and similar materials are often to be observed. Standards are likely to give details on sampling specifications necessary for acceptance-based material characteristics and lot size to mandate minimum number and weights of increments, gross (combined) sample weights, and other factors.

Selection of appropriate time intervals for increment extractions relates to property variation (inhomogeneity) within material flow streams. Ten minute extraction intervals are generally adequate to obtain suitably representative samples from material flows under practical circumstances. Precise determination of extraction intervals consistent with individual applications can be calculated through autocorrelation of historical sampling data, a statistical method described in references (Gy, Pitard).

Sample Quantity Reduction As sample increments are accumulated by multiple extractions from a bulk flow of material, according to the parameters of sampling to accommodate material stratification and nonhomogeneous composition, gross sample quantities (primary sample) often become quite extensive. Large primary sample volumes are subject to mechanical resampling to obtain final samples of practical, reduced quantities for testing. The same principles of sampling applied to primary sampling are used to design resampling to accomplish sample reduction without loss of sample statistical validity.

Sample reduction in successive stages—primary to secondary, secondary to tertiary, etc.—can be fulfilled using automatic sampling equipment while observing design principles of statistical sampling. Alternatively, sample quantity reduction may be carried out in a laboratory.

Sample reduction by mechanical procedures in automatic on-line mode encompasses (1) particle-size reduction preceding a following stage of resampling, and (2) multiple secondary increments taken for each primary increment when resampling without particle-size reduction. Particle-size reduction implies crushing or grinding the sample before resampling. A sampling-unit design incorporating primary and successive stages of sampling, with particle-size reduction and controlled flow of sample through intermediate stages, is developed in accord with application requirements while maintaining specified standards of sample accuracy.

Calculation of Sample Extraction Increments Sample quantities taken in an extraction increment are calculated in accord with the mechanical sampler employed. The following three examples illustrate calculations for three commonly used sampling methods.

Example 5: Solids Sampling by Linear Traversing Trajectory Cutter Increment weight S by a linear traversing cutter from bulk material flow of fine powder B expressed in unit weight per unit time is calculated by

$$S = \frac{B \times D}{V} \quad \text{example } S = 1.38 = \frac{120 \times 2000 \times 0.375}{3600 \times 18}$$

where V is cutter velocity and D is cutter opening. For S given in 120 short tons per hour converted to lbs, 0.375-in cutter opening, and 18-inches-per-second cutter speed, each increment is 1.38 lb. For consistent units, tons per hour is multiplied by 2,000 for lbs per hour, and divided by 3,600 for lbs per second.

Example 6: Slurry Sampling by Rotary Traverse of Gravity Flow Increment volume, quantity of slurry extracted by one cutter rotation, is S from bulk slurry flow B expressed in volume-per-unit time. R is cutter rotation per minute. D is cutter angle opening, with $D/360$ extraction ratio for continuous cutter rotation.

$$S = \frac{D \times B}{360 \times R} \quad \text{example } S = 0.055 = \frac{2.5 \times 200}{360 \times 25}$$

with S gallons per extraction for 200 gallons per minute, 2.5 degree cutter opening, and 25 RPM cutter rotation rate.

Example 7: Cross-Belt Sampling of Solids from Conveyors Increment weight is S from bulk material flow B expressed in unit weight per unit time. J is belt speed in length-per-unit time. $J \times 2$ is cutter speed. Therefore, cutter angle determining path length through material loads on the conveyor belt is 30 deg for traversing perpendicular to direction of conveyor movement. Extraction weight is corrected by csc(30 deg) to account for diagonal path of the cutter. Solids weight-per-unit length of conveyor belt is B/J. With cutter width D of 50 mm, minimum recommended for fine powders, increment weight S is

$$S = \frac{B \times D \times 1.16}{J} \quad \text{example } S = 1.93 = \frac{120 \times 1000 \times 50 \times 1.16}{3600 \times 1 \times 1000}$$

for S given in kg at 120 metric tons per hour and 1 meter per second conveyor belt speed. Consistent units require tons per hour be multiplied by 1,000 for kg per hour, and divided by 3,600 for kg per second. Cutter opening is divided by 1,000 for meters.

Sampling Trajectory Stream from Conveyor-Belt Discharge Conveyor-belt speeds above approximately 300 ft per minute (1.5 meters per second) impart sufficient momentum to material discharging at its head pulley to cause lifting of material streams in a trajectory from the head pulley. A trajectory is illustrated in Fig. 19-7. Blades of the sample cutter are positioned to intersect the trajectory. See Fig. 19-7 for an example of a linear-traversing bottom-dump cutter installation. Calculation of trajectory profiles are described in the Conveyor Equipment Manufacturers Association publications and similar references.

SAMPLING EQUIPMENT COST DATA

The cost of an electric-drive rotary-cutter sample of the smallest size manufactured—suitable for gravity sampling of fine particulate solids or slurry flow—including timer and control unit was approximately $5,000 in 1996.

An electric-drive linear-traversing sampler of minimum standard manufactured size with cutter and controls will range upwards of $8,000.

Pneumatic as well as electric-drive samplers are available. Generally, pneumatic-drive samplers are lower in cost.

Cross-belt samplers of minimum size for 24-in (600-mm) conveyors cost approximately $15,000 with controls using an electric drive, and about $12,500 with pneumatic drive.

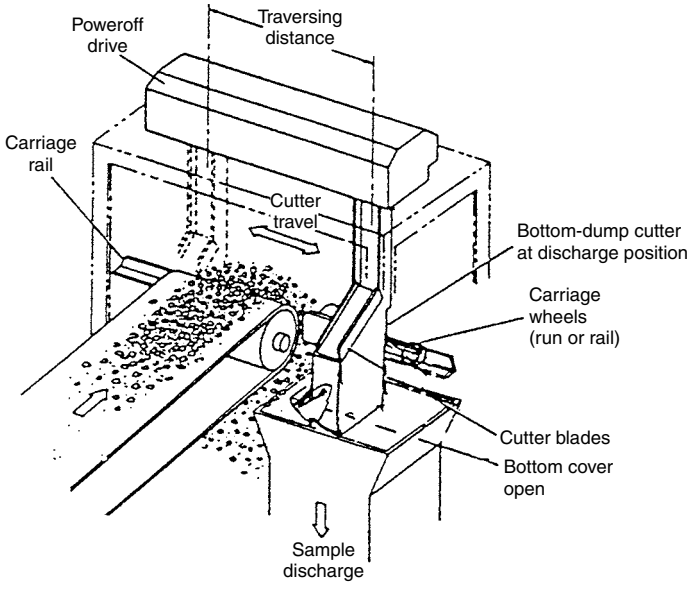


FIG. 19-7 Traversing linear bottom-dump sampler. (*Courtesy of Harrison R. Cooper Systems, Inc. Salt Lake City, Utah.*)

Hydraulic-drive samplers are also available, but cost factors tend to be substantially greater than electromechanical units. Recent use of hydraulic-drive systems has diminished with the availability of increased strength and durability electric-motor linear-drive units capable of reliable operation in high-capacity applications.

Sampling systems for multiple-stage sample reduction incorporating components such as crushing units, interstage feeders, reject handling, and others range up to several hundred thousand dollars in cost. A requirement would be rarely encountered in fine-powder applications.

SOLID-SOLID SYSTEMS

MIXING

General References

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A comprehensive bibliography is available in Ref. 9. A more recent update can be found in Ref. 18. Equipment photographs and details are available in Refs. 2, 4, 5, 7, 8, and 10. References 3 and 6 give excellent theoretical work. Reference 5 gives a tabulation and summary of many mixer types and applications. References 8 and 9 are book chapters dealing with mixing of solids and cover both the theoretical and the equipment aspects. Interpretive summaries of the literature in various areas (state of mixedness, theoretical frequency distributions, rate equations, and equipment) are included in Refs. 9 and 18. Reference 1 gives a procedure for testing solids-mixing equipment.

Fundamentals

Objectives Equipment in which solid materials are mixed may be used for a number of operations. Blending of ingredients may be the main objective, as, for example, in the preparation of feeds, insecticides, fertilizer, glass batches, packaged foods, and cosmetics. Other objectives may include cooling or heating such as in the cooling of limestone or sugar or the preheating of plastic prior to calendering. Drying or roasting of the solids is sometimes desired. In some applications, such as polymerization of plastics, catalyst manufacture, or the preparation of cereal products, the solids mixture may be reacted. Coating is desired in some cases, as in the manufacture of pigments, dyes, minerals, candy, and other food products and in the preparation of feeds. In certain of these cases, small amounts of liquid may be added, but the end product is a solids mixture. Sometimes agglomerates are desired, as in the preparation of food products, pharmaceuticals, detergents, and fertilizer. Often size reduction is desired while solids are being mixed. In all cases, the mixing of solids occurs. However, in some of these operations, the details of the equipment to accomplish operations other than pure blending may become a major problem. This portion of Sec. 19 will deal with equipment whose major function is to give a thorough mixture of solids. Specialized equipment to perform the other functions is discussed in other sections of the *Handbook* and will not be dealt with here. Thus, for example, Sec. 8 is devoted to size reduction and enlargement, although equipment mentioned there may also accomplish mixing.

Properties Affecting Solids Mixing Wide differences among properties such as particle-size distribution, density, shape, and surface characteristics (such as electrostatic charge) may make blending very difficult. In fact, the properties of the ingredients dominate the mixing operation. The most commonly observed characteristics of solids are as follows:

1. *Particle-size distribution.* This tells the percentages of the material in different size ranges.
2. *Bulk density.* This is the weight per unit of volume of a quantity of solid particles, usually expressed in kilograms per cubic meter (pounds per cubic foot). It is not a constant and can be decreased by aeration and increased by vibration or mechanical packing.
3. *True density.* The true density of the solid material is usually expressed in kilograms per cubic meter (pounds per cubic foot). This, divided by the density of water, equals specific gravity.
4. *Particle shape.* Some types are pellets, egg shapes, blocks, spheres, flakes, chips, rods, filaments, crystals, or irregular shapes.
5. *Surface characteristics.* These include surface area and tendency to hold a static charge.
6. *Flow characteristics.* Angle of repose and flowability are measurable characteristics for which standard tests are available (e.g., ASTM Test B213-48, Flow Rate of Metal Powders, etc.). A steeper angle of repose would indicate less flowability. The term "lubricity" has sometimes been used for solid particles to correspond roughly to viscosity of a fluid.
7. *Friability.* (Also see "Grindability," Sec. 8.) This is the tendency of the material to break into smaller sizes in the course of handling. There are quantitative tests specially devised for certain materials such as coal which can be used to estimate this property. Abrasiveness of one ingredient upon another should also be considered.
8. *State of agglomeration.* This refers to whether the particles exist independently or adhere to one another in clusters. The kind and degree of energy employed during mixing and the friability of the agglomerates will affect the extent of agglomerate breakdown and particle dispersion.
9. *Moisture or liquid content of solids.* Often a small amount of liquid is added for dust reduction or special requirements (such as oils for cosmetics). The resultant material may still have the appearance of a dry solid rather than a paste.
10. *Density, viscosity, and surface tension.* These are properties at operating temperature of any liquid added.
11. *Temperature limitations of ingredients.* Any unusual effects due to temperature changes which might occur (such as heat of reaction) should be noted.

A look at these properties for the ingredients to be mixed is a first step toward selecting mixing equipment.

Measuring Uniformity Except for cases in which a coating of one ingredient with another takes place, the theoretical end result of mixing will not be an arrangement in which one type of particle is directly next to a different type. Rather, the theoretical end result when random tumbling takes place will be a random mixture along the lines shown in Fig. 19-8.

The variation among spot samples of known size can be predicted theoretically for a random mixture and used as a guide to determine how closely random blending of the ingredients has been approached. Various types of analyses can be made on spot samples to determine batch uniformity. These could include x-ray fluorescence, flame spectrometry, polarography, emission spectroscopy, and so on, depending on the powder being examined. Radio-tracing techniques may also be appropriate. As many spot samples as possible should be analyzed. These should be taken at random from different locations in the batch. Sample size is an important consideration and is discussed below.

Evaluation Statistical tests can be used to evaluate relative homogeneity based on observed variations in spot sample composition. For a simple binary mixture such as that shown in Fig. 19-8, it can be shown (see Ref. 9) that the expected variance among samples containing n particles each is given by

$$\sigma^2 = \frac{p(1-p)}{n} \tag{19-1}$$

where p is the overall fraction of black (or white) particles in the mixture. The observed sample variance can be computed using

$$S^2 = \frac{1}{m-1}\left[\sum_{i=1}^{m} p_i^2 - \frac{1}{m}\left(\sum_{i=1}^{m} p_i\right)^2\right] \tag{19-2}$$

where p_i is the fraction of black (or white) in the ith sample and m is the total number of samples taken. The expected and observed variances can be compared using the statistical F-test (see Sec. 2 or any standard reference on statistics) which determines the likelihood that the F-ratio (S^2/σ^2) could be obtained from a random mixture, purely by chance.

The procedure can be readily extended to multicomponent systems by applying the test to each component in turn. In real systems, it is generally convenient to take samples of fixed volume or mass rather than fixed number of particles. In such cases, the expected variance can be computed using (see Refs. 19 and 20)

$$\sigma^2 = \frac{f_{ij}(1-f_{ij})w_{ij} + f_{ij}^2(\overline{w} - w_{ij})}{M} \tag{19-3}$$

where f_{ij} is the overall mass fraction of size i composition j material in the mixture, M is the sample mass, w_{ij} is the mass of a single particle of size i composition j and $\overline{w}$ is the mean particle mass:

$$\overline{w} = \sum_i \sum_j f_{ij} w_{ij} \tag{19-4}$$

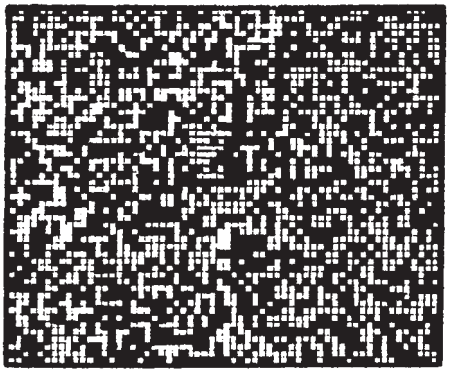


FIG. 19-8 Random arrangement of black and white particles. [*Lacey,* Trans. Inst. Chem. Eng. (London), ***21,*** *52 (1943).*]

The test for homogeneity is based on the probability of including different kinds of particles in a sample. For large samples, containing many particles, the expected variance given by Eq. (19-3) becomes extremely small and will often be exceeded by the variance due to experimental (analytical) error. The approach described above is, therefore, appropriate only for evaluating homogeneity at a scale approaching the size of the individual particles. If information at that scale is needed, it is necessary to use extremely small samples, containing no more than some hundreds of particles each. For very fine powders, this may seriously limit the choice of analytical techniques.

The use of very small samples to evaluate fine-scale homogeneity will often tend to mask long-range but small variations in composition. The use of somewhat larger samples is appropriate for detecting and quantifying such variations. In such cases, the sample variance can be compared, using the F-test, with an experimental variance S_E^2 obtained from replicate testing of the analytical procedure used to determine sample composition.

In general, a two-level procedure is recommended in which very small samples are used to evaluate microhomogeneity at the individual particle scale and larger samples are employed to investigate longer range variability. The actual sample sizes should be chosen such that microhomogeneity is evaluated from samples for which σ^2, as calculated using Eq. (19-3), is substantially less than the experimental (analytical) variance S_E^2 while macrohomogeneity is tested using samples with $\sigma^2 >> S_E^2$.

Whether the desired end product is satisfactory can also be used as a practical criterion of the adequacy of the solids mixture. A further consideration is the effect of the solids mixture on the overall economics of the manufacturing process. Studies of the type mentioned in the preceding subsection *may* be part of such an evaluation. When the solids mixture is made directly into a product, as in the case of feed pellets or pharmaceutical tablets, uniformity tests on these items will speak for themselves. If the solids mixture must be further processed, as in the manufacture of glass or plastics, the efficiency and costs of the subsequent operations can often be related to the starting solids mixture. In such cases, knowledge of the homogeneity of the solids mixture is needed to determine its effect on the manufacturing process.

Regardless of the method of evaluating the solids mixture, the sampling procedure is vital. Often a sampling thief, or other special device, is used to remove samples from the mixture without excessive disturbance of the batch. If an easier method of sampling is obvious and will bring less contamination to the batch, it should be used.

Method of sampling, location, size and number of samples, method of sample analysis, and fraction of the batch removed for sampling all contribute to how well the sampling study reflects the actual conditions.

A standard testing procedure for solids-mixing equipment is available (Ref. 1). This contains details and references pertaining to sampling from solids mixtures for both batch and continuous mixing.

Segregation Problems Previously it was pointed out that wide differences among properties may make blending very difficult. For example, natural segregating tendencies will be observed with extreme differences in specific gravity, size, or shape. The heavier, smaller, or smoother and rounder particles tend to sink through the lighter, larger, or jagged ones respectively. In some cases, preparation of the materials to avoid extreme differences in such ingredient properties can avoid segregation problems.

There are also other factors which can cause segregation.

Electrostatic charges may cause particles to repel each other. When continued blending may cause such charges to build up, it is important to determine the precise blending time required and not to overblend.

Loss of material as dust must be considered as a possible means of segregation and should not be aggravated by too strong suction in the dust-collection apparatus.

If there are smeary particles which have an almost pastelike behavior and barely flow (high angle of repose), frictional anchorage of these onto the other particles in the mixture may be necessary in order to achieve good mixing.

If a batch ingredient is in agglomerate form, some device to break up the agglomerates should be used to prevent them from segregating

from the rest of the mixture and to ensure the intimate dispersion of this ingredient throughout the mixture.

The use of a liquid such as water (possibly with a surface-active agent) can have remarkable effects in overcoming segregation which may appear inevitable otherwise.

Although these statements apply to the actual solids-mixing operation, thought must also be given to the subsequent processing steps. Thus, the solids-mixing operation must be checked from the point of view of delivering a well-mixed batch to a certain point. The system must be scrutinized for possible segregating points such as transfer points, long drops, flow through silos, and vibratory equipment. Where a liquid is used, the amount that can be added without getting into caking problems which may upset the later processing of the solids mixture should be determined.

Equipment

Mixing Mechanisms There are several basic mechanisms by which solid particles are mixed. These include small-scale random motion (diffusion), large-scale random motion (convection), and shear.

Motions which increase the mobility of the individual particles will promote diffusive mixing. If there are no opposing segregating effects, this diffusive mixing will in time lead to a high degree of homogeneity. Diffusive mixing occurs when particles are distributed over a freshly developed surface and when individual particles are given increased internal mobility. A plain tumbler gives the former, while an impact mill gives the latter.

For most rapid mixing, in addition to diffusive (fine-scale) mixing, there should be a means by which large groups of particles are intermixed. This can be accomplished by either the convective or the shear mechanism. A ribbon mixer illustrates the former, whereas a plain tumbler gives the latter.

The diffusion mechanism occurs readily for free-flowing powders in which individual particles are highly mobile, but is inhibited by cohesion among particles. It follows that cohesive powders, containing fine material or liquid phases, are relatively difficult to mix. At the same time, reduced particle mobility inhibits demixing so that once mixed, cohesive powders tend to remain so. Free-flowing powders, on the other hand are prone to demixing during any transport/handling operation. The beneficial effects, noted above, of liquid addition presumably result from increased cohesion.

Types of Solids-Mixing Machines There are several types of solids-mixing machines. In some machines the container moves. In others a device rotates within a stationary container. In some cases, a combination of rotating container and rotating internal device is used. Sometimes baffles or blades are present in the mixer. Most types can be quite effective for free-flowing powders, bearing in mind that segregation may also be favored. Highly cohesive powders generally require high shear (velocity gradient) to achieve a high degree of microhomogeneity. Table 19-1 classifies solids-mixing machines via the characteristics given in the column headings. Illustrations of several of the machines listed there are shown in Fig. 19-9. The various types listed in Table 19-1 will be briefly discussed, with paragraph numbers referring to the columns.

1. *Tumbler.* Suitable for gentle blending; capable of handling large volumes; easily cleaned; suitable for dense powders and abrasive materials. Not for breaking up agglomerates.

Figure 19-9*a* and *b* (without broken-line portions) shows some unbaffled tumblers.

Figure 19-9*c* and *d* shows some baffled tumblers.

2. *Tumbler with agglomerate breaker.* See Sec. 20: "Tumbling Mills," for ball mill, rod mill, and vibratory pebble mill which will accomplish mixing along with size reduction.

Several tumblers are available with separately driven internal rotating devices for breaking up agglomerates. The tumbler itself can be used for gentle blending if agglomerate breakdown is not required.

The broken-line portions of Fig. 19-9*a* and *b* show some types of agglomerate-breaking devices for tumblers.

Table 19-2 includes impact velocities for some internal rotating devices in tumblers as well as other mixers. Contamination and wear problems of internal rotating devices are discussed under "Performance Characteristics."

3. *Stationary shell or trough.* There are a number of different types of mixers in which the container is stationary and material displacement is accomplished by single or multiple rotating inner mixing devices.

a. Ribbon mixer (Fig. 19-9*e*). Within this subgroup there are several types. Ribbon cross section and pitch, clearances between outer ribbon and shell, and number of spirals on the ribbon are some features which can be varied to accommodate materials ranging from low-density finely divided materials that aerate rapidly to fibrous or sticky materials that require positive discharge aid. Other construction variations are center or end discharge and the mounting of paddles or cutting blades on the center shaft. A broad ribbon can be used for lifting as well as for conveying, while a narrow one will cut through the material while conveying. The ribbon is adaptable to batch or continuous mixing.

b. Vertical screw mixer. This subgroup also has several variations. One type is shown in Fig. 19-9*f*. In this type, the screw rotates

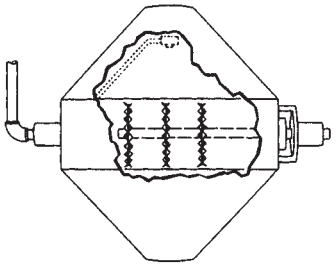
TABLE 19-1 Types of Solids-Mixing Machines*

Tumbler (1)	Tumbler with internal agglomerate breaker (2)	Stationary shell or trough (3)	Both shell and internal device rotate (4)	Impact mixing (5)	Process steps which can affect solids mixing‡ (6)
Without baffles:					
Drum, either horizontal or inclined	Ball mill Pebble mill	Ribbon	Countercurrent, muller turret and pan rotate in opposite directions	Hammer mill	Filling of hoppers
Double cone	Rod mill	Stationary pan, rotating muller turret†		Impact mill	Fluidization
Twin shell Cube	Vibratory pebble mill	Vertical screw	Planetary types	Cage mill	Screw feeders
Mushroom type	Double cone Twin shell Cube	Single rotor Twin rotor		Jet mill Attrition mill	Conveyor-belt loading Elevator loading
		Turbine Paddle mixer			Pneumatic conveying Vibrating
With baffles:					
Horizontal drum		Sifter (turbosifter)			
Double cone revolving around long axis					

* Diagrammatic sketches of many of these machines are shown in Fig. 19-9.

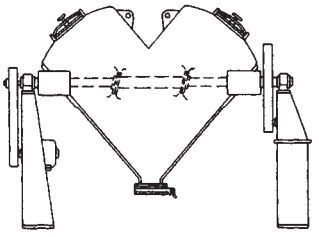
† There is also a muller in which the turret is stationary but the pan rotates.

‡ Although these steps, when carefully selected, can aid mixing, caution must be exercised with pneumatic conveying and vibrating, as they may tend to separate materials.



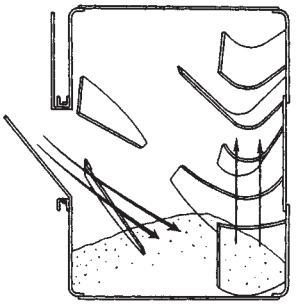
(a) Double cone

Agglomerate breaking device shown in broken line. Spray nozzle shown in dotted line. Tumblers of this type available plain or with either or both of the above features.

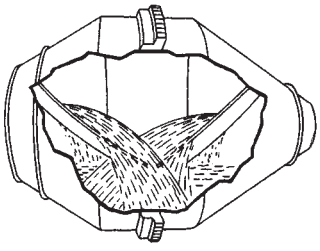


(b) Twin shell (Vee)

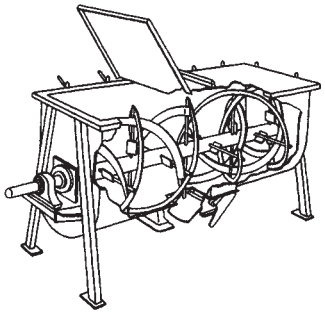
Agglomerate breaking and liquid feeding device shown in broken line. Where no liquid feeding is necessary, a pin-type agglomerate breaking device is used. Tumblers of this type are available plain or with any of the above features.



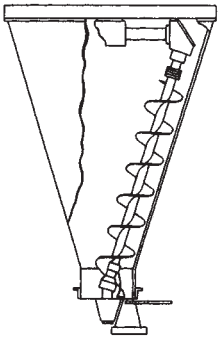
(c) Horizontal drum (with baffles)



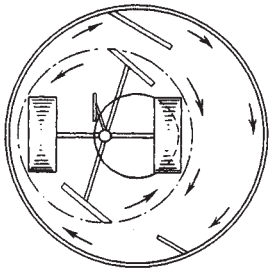
(d) Double-cone revolving around long axis (with baffles)



(e) Ribbon

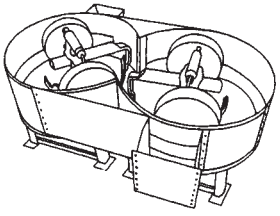


(f) Vertical screw (orbiting type)

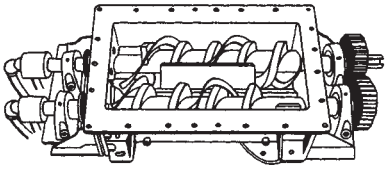


(g) Batch muller

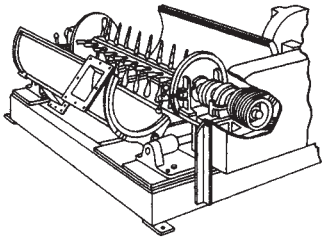
Three types are available:
(1) pan is stationary and muller turret rotates;
(2) muller turret is stationary and pan rotates;
(3) pan rotates clockwise, muller turret rotates counterclockwise.
Type 3 is illustrated above



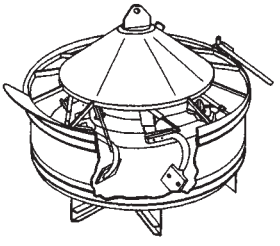
(h) Continuous muller (stationary shell)



(i) Twin rotor (adapted to heat transfer-jacketed body and hollow screws)



(j) Single rotor



(k) Turbine

FIG. 19-9 Several types of solids-mixing machines. (See Table 19-1).

TABLE 19-2 Approximate Impact Velocities of Some Rotating Internal Devices in Mixers*

Type of mixer (see Table 19-1)	Tip speed, ft/min
Ribbon	280
Turbine	600
Twin-shell tumbler with	
Pin-type intensifier	1700
Liquid-feed bar	3300
Twin rotor	Up to 1300
Single rotor	6000–9000
Mills of various types	2500–20,000

*To convert feet per minute to meters per second, multiply by 0.00508.

about its own axis while also orbiting around the center axis of the conical tank. In another variation, the screw does not orbit but remains in the center of the conical tank and is tapered so that the swept area steadily increases with increasing height. In another type, the central screw is contained in an inner cylindrical casing. This type of mixer is primarily suitable for free-flowing dry solids.

c. Muller mixer. The stationary-pan muller with rotating turret is one of several types. Other muller types are the countercurrent type, in which the pan and muller turret rotate in opposite directions, and the rotating-pan type, in which the muller turret is stationary.

The heavy, wide roller rides over the material. There is some skidding action where the rollers engage the mass of materials. This gives local shearing plus coarse-scale mixing which is aided by the plows and scrapers.

The muller is useful for mixing problems requiring certain types of aggregate breakdown, frictional anchorage of particles to one another, and densification of the final mix. Materials which are excessively fluid or sticky should be avoided. The muller mixer is generally used for batch operations (Fig. 19-9*g*), although Fig. 19-9*h* shows a continuous muller.

d. Twin rotor (Fig. 19-9*i*). This consists of two shafts with either paddles or screws encased in a cylindrical shell. There are various types available with shaft speeds ranging from moderately low to relatively high (see Table 19-2). The twin rotor is useful for continuously mixing non-free-flowing solids; liquids can be added, there is minor product attrition, and materials can be added beyond the inlet. It is easily adaptable to heating or cooling. Some machines are specifically designed for heat transfer during mixing. The pug mill is one type of twin rotor.

e. Single rotor (Fig. 19-9*j*). This consists of a single shaft with paddles encased in a cylindrical shell. This type is available with relatively high speeds (see Table 19-2), although in certain cases lower speeds are used. A high-speed single rotor gives the maximum impact short of a grinding mill. It is used for intensive dispersion and disintegration. The type is available with split casing and is suitable for heating or cooling and for small amounts of liquid addition.

f. Turbine mixer (Fig. 19-9*k*). This is a circular trough with a housing in the center around which revolves a spider or a series of legs with plowshares or moldboards on each leg. The moldboards spin around through the circular trough. This mixer is suitable for free-flowing dry materials or semiwet materials which do not flow well and is also adaptable to liquid-solid mixing and coating problems.

4. *Shell and internal device rotate.* The countercurrent muller (Fig. 19-9*g*), which is in this category, is mentioned under "Muller mixer." This machine has a clockwise rotating mixing pan with a counterclockwise rotating mixing tool head mounted off center of the pan, thus providing a planetary mixing pattern. For the mixing of free-flowing solids not requiring the shearing and compressive action of mullers, plows are sometimes used alone. When used with mullers, plows deflect material into their path. Special mixing tools are also available.

5. *Impact mixing.* This process, which includes size reduction, is covered in Sec. 20.

The process steps listed in Table 19-1 can sometimes be used to promote mixing. However, they are primarily for functions other than solids mixing. (Note precautions for pneumatic conveying and vibrating in Table 19-1.)

Since paste mixing is not within the scope of this section, such widely used paste mixers as the sigma blade and banbury types will not be covered here but instead are discussed in Sec. 18.

Performance Characteristics Before selecting solids-mixing equipment, a careful study should be made of various performance characteristics. These are given here.

Uniformity of Mixture The proper type of mixer should be chosen to assure the desired degree of batch homogeneity. This cannot be compromised for other conveniences. Information is given under "Types of Solids-Mixing Machines" about the special abilities of various kinds of machines to blend different types of materials.

Care should be taken to avoid mixing too long, as in some cases this will result in a poorer blend. A graph of degree of mixing versus time should be made to select the proper mixing time quantitatively.

Mixing Time The actual time during which the batch is being mixed is usually less than 15 min if the proper type of machine and working capacity have been chosen. In some cases much more lengthy mixing times are tolerated so as to avoid the cost of purchasing more efficient equipment. However, there is usually a machine that can properly homogenize almost any type of mixture in less than 15 min provided one is willing to pay the price. In fact, proper mixer design in most instances will produce the desired blend in a few minutes.

Besides actual mixing time, however, the total cycle time should be optimized.

Charging and Discharging The total handling system must be considered in order to obtain optimum charging and discharging conditions. This includes the efficient use of weigh hoppers and surge bins, minor-ingredient premixing, location of discharge gates, and so on.

Power In general, power requirements are not a major consideration in choosing a solids mixer since other requirements usually predominate. However, sufficient power must be supplied to handle the maximum needs should there be changes during the mixing operation. Also, when a variety of mixes may be required, power must be sufficient for the heaviest bulk-density materials. If the loaded mixer is to be started from rest, there should be sufficient power for this. When speed variation may be desirable, this should be taken into account in planning power requirements.

Horsepower requirements of several types of mixers are listed in Table 19-3.

Cleaning The ease, frequency, and thoroughness of cleaning may be crucial considerations when incompatible batches are to be mixed at different times in the same machine. Plain tumbling vessels are easy to clean provided that adequate openings are available. Areas that may present cleaning problems are (1) seals or stuffing boxes, (2) crevices at baffle supports, (3) any corners, and (4) discharge arrangement. If cleaning between different batches may be time-consuming, several small mixers should be considered. Special sanitary construction can usually be provided at extra expense.

Agglomerate Breakdown and Attrition The two methods of producing agglomerate breakdown and attrition are as follows:

1. *Impact.* The major factor is the peripheral speed of the rotating internal device. Table 19-2 gives impact-velocity data for various mixers.

2. *Shearing and compressive action.* In mullers this depends upon the clearance between muller and pan and the muller weight or spring load respectively.

When an attrition device is necessary to break down aggregates but may also produce too much size reduction on other batch ingredients, tolerable attrition should be determined by tests.

Dust Formation Loss of dust can seriously affect batch composition, particularly when vital minor ingredients are lost. Methods of minimizing dust formation are: (1) Use of less dusty but equally satisfactory batch ingredients. Sometimes a pelletized form of an extremely dusty material is available. (2) Proper venting so as to enable filtering of displaced air rather than unregulated loss of dust-laden air. (3) Dust-tight arrangements for loading and unloading the mixer. (4) Addition of liquids if tolerable. Not only is water effective in minimizing dust upon discharging from the mixer, but if properly added it will also render the batch less dusty in subsequent handling steps. The addition of a small quantity of surface-active agent will improve the penetration of the water throughout the batch and enable

TABLE 19-3 Horsepower Requirements and Speeds of Rotation for Some Commercial Solids Mixers

[Approximately 1.5 m^3 (50 ft^3) Working Capacity]

Type of solids-mixing machine	Approximate working capacity, ft^3	Horsepower, hp		Rotational speed, r/min		Comments
		Shell	Internal device	Shell	Internal-device shaft speed	
1. Tumbler						
Without baffles						
Double cone	54	7½		18		Based on 100-lb/ft^3 material.
Twin shell	50	5		13.7		Maximum bulk density of material = 55 lb/ft^3.
With baffles						
Horizontal drum						
Manufacturer E	50	20		11.1		Heavy-duty (material 100 lb/ft^3). For extremely heavy duty (150–200-lb/ft^3 material), the maximum working capacity with 20-hp motor is 35 ft^3.
Manufacturer F	50	10		14		For material of 40-lb/ft^3 maximum bulk density.
Double cone revolving about horizontal axis	56	25		11.5		Mixer can be tilted. Rear end charger. Capacity based on mixed concrete.
2. Tumbler with agglomerate breaker						
Double cone	54	7½	See Comments.	18	See Comments.	Horsepower requirement for internal device depends on character of material, type, and speed of agitator. These are to be determined by adequate testing.
Twin shell	50	5	5 (pin-type intensifier bar) 7½ (liquid-solids intensifier bar)	13.7	945 (1730-ft/min tip speed) 1055 (3320-ft/min tip speed)	Maximum bulk density of material = 55 lb/ft^3.
3. Stationary shell or trough						
Ribbon						
Manufacturer C	50		12		28	Horsepower required based on material of 50–60-lb/ft^3 bulk density, medium free-flowing, using 10 hp/ton for average mix cycle of 3–10 min (depending on material, range can be 3–18 hp/ton).
Manufacturer A	46		10		37	Based on material of 30-lb/ft^3 bulk density.
Manufacturer D	50		15		45	Based on material of 40–50-lb/ft^3 bulk density.
Three-shaft ribbon	50		Blender shaft 20 Feeder shaft 7½ (total)		Variable-speed drives on all shafts	This blender is rated at 300 ft^3/h on batch-mixing basis; 900 ft^3/h on continuous-mixing basis. Materials rated at 70-lb/ft^3 bulk density.
Vertical screw	52.9		5		Screw, 64.4 Orbit, 2.2	Horsepower based on 37-lb/ft^3 bulk density. This may vary with different materials. Maximum hp = 10, maximum weight = 4410 lb.
Muller:						
Batch; stationary pan, rotating turret	40		60		24 (turret speed)	Based on material of 60–75-lb/ft^3 bulk density.
Continuous; stationary pan, rotating turret	Basically, the continuous mullers are merely two-batch mullers joined together at the cribs, making a figure-8 design. Thus, the 40-ft^3 batch muller rated at 60 hp becomes an 80-ft^3 working-capacity continuous muller requiring 125 hp. This would give 125 tons/h with a 2½-min residence time. Turret speeds are 24 r/min.					
Single rotor		See Comments.				In this *continuous* unit, output can range from 25–600 lb/min with hp from 5 to 100 and r/min of 500 to 4000, depending on the materials mixed.
Double rotor		See Comments.				In this *continuous* unit the output can range from 200–500 lb/min with hp from 5 to 40 and r/min from 200 to 300, depending on the materials mixed.
Twin-rotor heat-exchanger mixer	49.2		5–15		20–100	Amount of conveying and mixing action affected by amount of pitch and type of ribbons mounted on exterior of hollow screws.
Turbine	50		50		Peripheral speed of 600 ft/min	
4. Both shell and internal device rotate						
Countercurrent muller	45 60–90†	* 20	* 25	6.75–8.75 6.65	28–35 20	

*One 25-hp motor drives both the shell (mixing pan) and the internal device (mixing star).

†Batch-capacity range depends on nature of materials to be mixed.

NOTE: To convert cubic feet to cubic meters, multiply by 0.02832; to convert horsepower to kilowatts, multiply by 0.7457; to convert pounds per cubic foot to kilograms per cubic meter, multiply by 16.02; to convert tons per hour to kilograms per second, multiply by 0.252; to convert revolutions per minute to radians per second, multiply by 0.1047; to convert pounds per minute to kilograms per minute, multiply by 0.4535; and to convert horsepower per ton to kilowatts per metric ton, multiply by 0.8352.

it to wet even such materials as coal dust. The method of adding water is important (see "Method of Adding Liquids").

Care should be taken to avoid powerful suction or air flow on the mixer or the weigh hopper from which the ingredients feed into the mixer. If the dust-collection suction on the mixer is too strong, vital ingredients may be sucked out. If the dust-collection suction on the weighing system is too strong, errors in weighing may result.

Electrostatic Charge Certain batch materials such as plastics tend to accumulate a charge easily. Work input will affect the charge on the batch. Coating of the inside of the mixer shell or rotating elements may occasionally result because of electrostatic charge. This can present a cleaning problem. Possible aids in overcoming this are (1) addition of special solid materials with very high surface area to weight ratios, (2) addition of liquids (see "Dust Formation" and "Method of Adding Liquids"), (3) proper choice of material of construction of the mixer, (4) controlling humidity, (5) preparation of the batch ingredients so as to minimize accumulated charge.

Equipment Wear Simple tumbling mixers give the least wear. Attrition devices in tumblers may present serious abrasion problems with certain materials such as sand and abrasive grinding-wheel grains. Abrasion-resistant coating such as rubber coating, special alloys, or platings should be considered for these cases. An internal agitator device may wear even though its speed is low. Particularly when highly abrasive materials are to be mixed, the benefits of an agglomerate-breaking device must be weighed against potential contamination and replacement and maintenance costs.

Contamination of Product This has been partially covered under "Cleaning" and "Equipment Wear." Other sources of contamination are lubricants and repair materials. Types which are not compatible with the batches to be mixed should be avoided.

Heating or Cooling Nearly all commercial mixers can be heated or cooled. Some can be provided with heated or cooled agitators. If temperature rise during mixing is detrimental, cooling facilities should be provided. The various manufacturers can provide details on the means of heating their machines. Most common heating means are (1) water or steam in the jacket and in hollow-screw or paddle-type internal agitator, (2) hot oil, (3) Dowtherm liquid or vapor, (4) electric heaters, contact or radiant, (5) hot air in direct contact with product (suitable only for revolving-drum-type mixers), (6) exterior heating of drum by direct or indirect firing. For cooling, the most common means are (1) water or refrigerated fluid in the jacket and in hollow-screw or paddle-type internal agitator, (2) an evaporant such as liquid ammonia, (3) direct air contact (for rotating-shell mixers), and (4) oil or Dowtherm (or its equivalent) for cooling high-temperature materials.

Flexibility When batches of widely different size must be mixed, flexibility of operating capacity may enable use of fewer mixers. Certain features may necessitate a nonflexible capacity requirement. For example, ordinarily an internal agitating device in a tumbling mixer does not function effectively unless the batch is loaded to a certain level. The need for such features must be weighed against the limitations imposed by a narrow operating-capacity range when choosing equipment for an operation in which batch size will vary considerably.

In general, the effect of percentage of mixer volume occupied by the batch on the adequacy of mixing should be borne in mind, particularly when any change from the recommended volume percent is considered.

Vacuum or Pressure Most tumbling mixers can have provision for vacuum or pressure. Mixers which cannot be adapted to these conditions are mullers with rotating pans. Continuous mixers introduce problems of sealing the charge and discharge ends.

Method of Adding Liquids When the addition of liquids may be desirable (see "Dust Formation" and "Electrostatic Charge"), this should be considered when designing the mixing system rather than hastily improvised. The purpose of the liquid should be considered, whether for (1) dust suppression, (2) product, or (3) heating and cooling. If a viscous liquid must be well distributed, this requirement should be considered when choosing the mixer.

Liquid should be directed into the batch materials and not onto bare mixer surface since this could cause buildup. Nozzle spray pressure should be sufficient to penetrate the batch but not so high as to cause heavy splashing. The liquid should be added to the well-mixed batch. In particular, when premature addition of liquid could impair the adequacy of blending, both the time during which it is added in the mixing cycle and the time taken to add the liquid are important.

Automated equipment for the addition of liquids can be worked into the overall mixing plant when necessary. For dust-reduction purposes, a volumetric method of metering is satisfactory. However, should a critical batch ingredient be added in liquid form, a more precise method of metering may be necessary.

Other considerations are (1) proper ventilation and discharge enclosures, (2) provision for relief of internal explosion, (3) vibration isolation (shock mounts), (4) remote operation of charge and discharge, (5) noise during operation.

Equipment Selection Types of mixers and performance characteristics have been given. Segregating tendencies among solid materials have also been described. A sound approach to solids-mixer selection starts with a careful examination of these areas. However, mixer selection should also involve consideration of the mixer's place in the overall process. Possible consolidation of many solids-processing steps or the opposite (splitting one operation into several) deserves scrutiny at this time. If no one standard machine has all the necessary requirements, thought should be given to which machine can best be modified to achieve the most desirable combination of features. One should look at the overall process objectives as well as at equipment details when selecting a solids mixer.

Pilot Tests In some cases, it is possible to perform pilot tests on a small-scale version of the equipment to be used in production. Much useful information can be found here but the following must be borne in mind:

1. In general, the larger the pilot unit, the more reliable the prediction of large-scale performance. The pilot unit should be a prototype with all dimensions properly scaled down.
2. Published solids-mixing scale-up data are rare. Equipment suppliers can provide scale-up information for their particular types of equipment on the basis of experience. With geometrically similar tumblers, if the speeds are adjusted to give comparable motion and the mixer volume fraction occupied by the charge is the same, scale-up of results will be straightforward. The presence of a rotating internal device presents problems in the scaling up of clearances, blade area to mixture volume, and sizes and speeds of the rotating devices. For agglomerate breakers, the key factor in scaling up is impact velocity. Scale-up in cylinders is discussed on pages 290–292 of Ref. 9. Solids-processing scale-up is discussed in a paper by Sterret (*Chem. Eng.*, Sept. 21, 1959).
3. The actual process materials should be used if possible. If substitute materials must be used, they should have the same mixing characteristics. Tests with differently colored but otherwise identical beads can be misleading, and so can tracers. The reason is that the flow properties of the specific materials to be mixed in the plant may not be the same as these demonstration materials. Regardless of how the mixer contents appear to be moved around, the properties of the actual batch ingredients may cause segregation or other problems.
4. Differences in materials of construction between the pilot unit and the production unit should be considered. These may have a bearing on caking, abrasion, and electrostatic effects.

Continuous Mixing Although batch mixing has been the predominant method of mixing solids, consideration is being given to the use of continuous mixing in many industries. There are two types of continuous-mixing operations. The first type has a low holdup volume and will provide fine-scale blending of the particles via impact and shear elements such as are used in grinding machines. Some machines of this type are hammer, impact, cage, and jet mills. It is essential that the feed to these machines be properly proportioned and premixed to achieve a uniform product.

The second type of continuous mixer involves high holdup machines which contain agitating and conveying mechanisms. These rearrange the individual particles and also displace large volumes of material and move the batch through the machine. Mixers of this type can produce both fine-scale and coarse-scale blending. The ribbon-type mixer is frequently used for continuous mixing, although this is also used for batch mixing. A continuous muller mixer has been developed as shown in Fig. 19-9*h*.

The average composition of the stream leaving a continuous mixer is the same as the average of the added entering streams. Variations in proportions of the entering streams will be damped out by the mixing action of a continuous mixer. These effluent-stream variations will become smaller as average solids residence time is increased and the frequency of the variations increases.

Certain general criteria can be used to determine whether continuous flow will be beneficial. Continuous flow is worth consideration if (1) a single formulation can be run for an extended period, (2) the fluctuations of the outgoing product are within process requirements, (3) sufficiently accurate metering of ingredients can be achieved, (4) the rest of the process warrants continuous mixing. Continuous flow is of doubtful benefit if (1) frequent changes of formulations are anticipated, (2) fluctuations of product composition will be outside the permitted range, (3) the ingredients cannot be metered with the necessary level of accuracy, (4) complex temperature or pressure cycles are involved.

Sometimes a system of mixing and dispersing is composed of one or more batch units providing a feed to a continuous intensive dispersion unit. Another possibility would be a batch mixer and surge bin which provide a continuous feed to a final dispersion unit. Various combinations of this type with adequate sampling at the proper points may be used when continuous flow would be beneficial provided that certain features could be overcome.

OPTICAL SORTING

Difference in optical properties can be used as the basis to separate solids in a mixture. Optical properties include color, light reflectance, opacity, and fluorescence excited by ultraviolet rays or x-rays. Differences in electrical conductance can also be used for separation. With appropriate sensing, the particles in a moving stream can be sorted by using an air jet or other means to deflect certain particles away from the mainstream (Fig. 19-10). The lower limit of particle size is about 0.003 m (⅛ in); below this limit the process rate would be slow and equipment costs become exceedingly high.

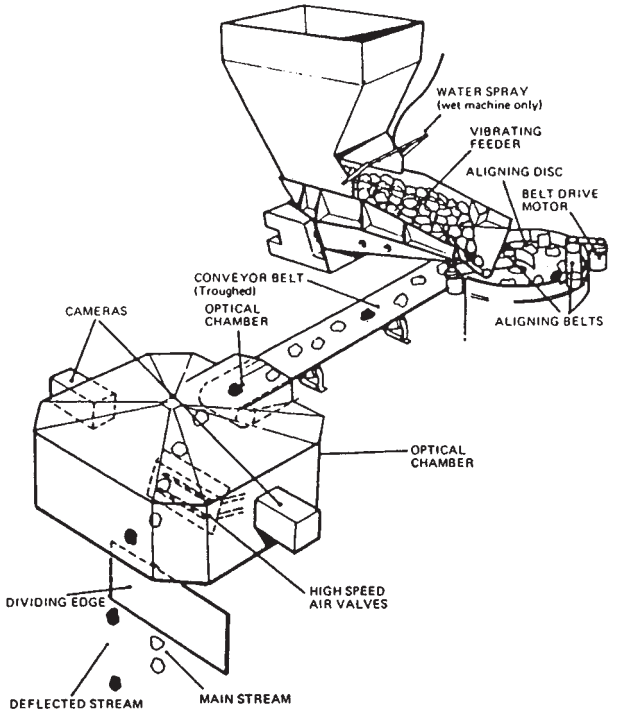


FIG. 19-10 Sortex 711M optical separator. (*Courtesy Gunson's Sortex Ltd.*)

In a typical **optical sorting** installation, the mixture of particles is fed from a hopper onto a vibrating feeder. Dust may be removed by dry screening or by water spray. The solids then enter a troughed conveyor belt and align the flow and cause the particles to be projected in a continuous stream along their free-fall trajectory. They are viewed in midair during fall through an optical chamber by a series of cameras arranged to view the entire surface of each particle. The color or reflectivity of the surface of each particle sets up a characteristic voltage pattern in the output circuit of a light-sensing photomultiplier. The patterns are analyzed electronically and compared with a preset reflectance level. When appropriate, a reject signal delayed electronically will activate on air jet to deflect a particle from the main stream.

An example of throughput is given in Fig. 19-11. For the machine referenced in Fig. 19-10, electronic sensing is capable of inspecting 80 particles per second.

Color sorting has been used for the recovery of glass from nontransparent materials in municipal solid waste. The separation of mixed glasses from opaques is illustrated in Figs. 19-12 and 19-13. As the throughput is increased, the glass recovery falls; and for any given installation there will be a breakeven point for the optimum number of machines against the amount of glass recovered. Color sorting can also separate mixed colored glasses to produce amber and green products that meet a specification of 10 percent contamination of one type of glass in the other.

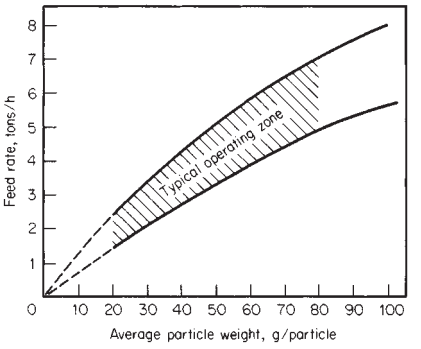


FIG. 19-11 Sortex 711M feed-rate characteristics. (*Courtesy Gunson's Sortex Ltd.*)

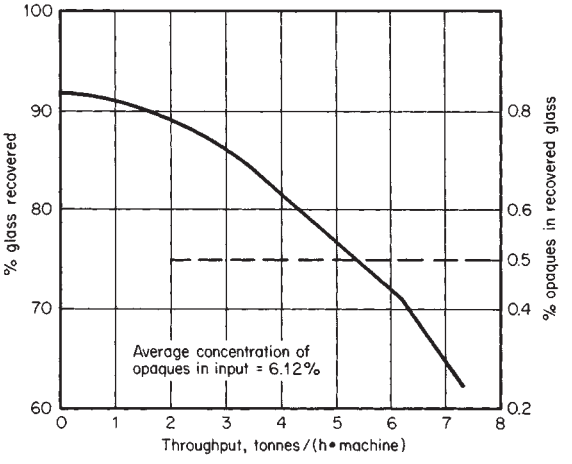


FIG. 19-12 Optical separation of mixed glasses: separation of opaques from glasses. (*Courtesy Gunson's Sortex Ltd.*)

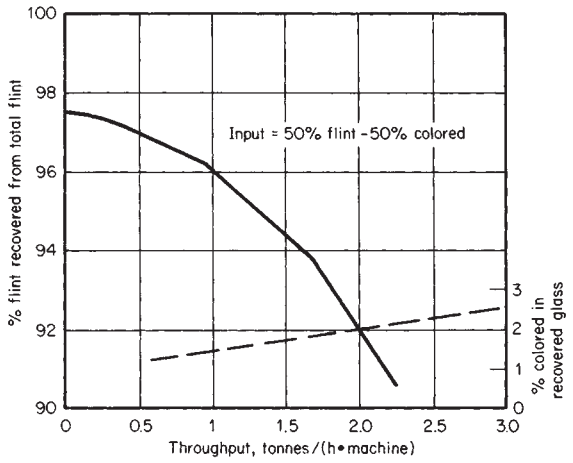


FIG. 19-13 Optical separation of mixed glasses: separation of flint from colored. (*Courtesy Gunson's Sortex Ltd.*)

When **electrical conductivity** is used as the basis of the sorting process, contact of the particles is made by a brush type of electrode to generate the signal for analysis. Materials having a resistance difference of 2000 kΩ can be readily separated from material of 100 kΩ resistance.

However, separation between resistance levels of 1000 to 300 kΩ may be marginal. A typical application of conductivity sorting is the separation of massive ilmenite from anorthosite. Both are compact rocks, but ilmenite is a good electrical conductor, whereas anorthosite is an insulator. The dimensions and operating information for the Sortex CS-03 conductivity sorter, which is capable of processing up to about 25,000 kg/h (27.5 tons/h) of 0.05- to 0.15-in mesh size (2 to 6 in), are given in Table 19-4.

The differences in absorptivity of radiant energy by different substances can also be used to separate materials. If a mixture of materials is exposed to radiant energy, for example, infrared, depending on the properties of the material involved, some particles will become heated more than others. The more opaque particles will be heated more by infrared heating than clear particles. Thus, the more opaque will become hotter. By spreading the irradiated material onto a surface coated with a low-melting thermoplastic or a heat-sensitive polymer, the higher-temperature particles will adhere, while the cooler particles will not. This is the basis for the **thermoadhesive-separation** method of Brison ("Separation of Materials," U.S. Patent 2,907,456, 1959) used by the International Salt Co. for removing impurities from mined rock salt. The heat-sensitive resin employed is a mixture of polymerized styrene resins, Piccolastic A-25 and Piccolastic A-50. The proportion of each was adjusted to give the required softening point to achieve the desired results. In practice, the resin can be continuously applied to a moving belt by brush or hot spray. Periodic scrapping and redressing are required to maintain belt performance.

Use of specific forms of radiant energy, infrared, ultraviolet, dielectric heating, etc., can allow specific separations to be made. The separation of clear and colored grains of glass and the separation of different metals are possible applications of the thermoadhesive method being considered in the field of solid-waste processing.

SCREENING

GENERAL REFERENCES: Beddow, "Dry Separation Techniques," *Chem. Eng.,* **88,** 70 (Aug. 10, 1981). Colman, "Selection Guidelines for Size and Type of Vibrating Screens in Ore Crushing Plants," in Mular and Bhappu (eds.), *Mineral Processing Plant Design,* 2d ed., Society of Mining Engineers, AIME, New York, 1980. Kuenhold, "Factors to Consider in Vibrating Screen Installations," *Min. Eng.,* 650–653 (June 1957). Matthews, *Chem. Eng.,* deskbook issue, **99** (Feb. 15, 1971). Matthews, "Screening," *Chem. Eng.,* **79,** 76 (July 10, 1972). Moir, "Recent Developments in Mineral Processing and Their Implications," *Economics of Mineral Engineering Mining Journal,* Books Ltd., London, 1976, p. 125. Mular, *Mineral Processing Equipment Costs and Preliminary Capital Cost Estimations,* spec. vol. 18, Canadian Institute of Mining and Metallurgy, Montreal, 1978. Pryor, *Mineral Processing,* 3d ed., Elsevier, New York, 1965. Reed, "The Story behind the New Sieve Specifications," *Test. World,* October 1959. Taggart, *Handbook of Mineral Dressing,* 2d ed., Wiley, New York, 1945.

TABLE 19-4 Specifications for Sortex Conductivity Sorter CS-03*

Dimensions	Height (excluding feeder), 1.7 m (70 in) Width, 1.9 m (76 in) Length, 2.5 m (100 in) Diameter of disk, 1.50 m (49 in)
Electric power	380–440 V, three-phase 50/60 Hz; consumption, 2 kW (excluding vibrating feeder)
Air consumption (depending on rejection rate)	7 m^3/min at 6 bar (250 ft^3/min at 80 lbf/in^2)
Water supply	4 L/min (1 gal/min) for cleansing the light source
Net weight	560 kg (22 cwt) approximately

*Courtesy of Gunson's Sortex Ltd.

Definitions

Screening Screening is the separation of a mixture of various sizes of grains into two or more portions by means of a screening surface, the screening surface acting as a multiple go-no-go gauge and the final portions consisting of grains of more uniform size than those of the original mixture.

Material that remains on a given screening surface is the oversize or plus material, material passing through the screening surface is the undersize or minus material, and material passing one screening surface and retained on a subsequent surface is the intermediate material.

The screening surface may consist of woven-wire, silk, or plastic cloth, perforated or punched plate, grizzly bars, or wedge wire sections.

Classification of screening operations and the range of separations that can be attained with various screens were given in concise form by Matthews (op. cit., 1971). See Table 19-5. Further details are given under "Equipment." Figure 19-14 indicates the size-range applicability of various screen types.

Mesh and Space Cloth Wire cloth is generally specified by "mesh," which is the number of openings per linear inch counting from the center of any wire to a point exactly 25.4 mm (1 in) distant, or by an opening specified in inches or millimeters, which is understood to be the clear opening or space between the wires. Mesh is generally favored for cloth 2 mesh and finer and clear opening for space cloth of 12.7-mm (½-in) opening and coarser.

Aperture Aperture, or screen-size opening, is the minimum clear space between the edges of the opening in the screening surface and is usually given in inches or millimeters.

Open Area The open area of a screen is the percentage of actual openings versus total screen area and can be determined by the formulas given in Fig. 19-22.

Particle-Size Distribution This is defined as the relative percentage by weight of grains of each of the different size fractions represented in the sample. It is one of the most important factors in evaluating a screening operation and is best determined by a complete size analysis using testing sieves.

Sieve Scale A sieve scale is a series of testing sieves having openings in a fixed succession; for example, in the original basic Tyler standard sieve scale the widths of the successive openings have a constant ratio of the square root of 2, or 1.414, while the areas of the successive openings have a constant ratio of 2. The Tyler scale has been enlarged to include intermediate openings so that the entire scale has successive openings according to the fourth root of 2, or 1.189. The sieve series adopted by the National Bureau of Standards, American Society for Testing and Materials, American National Standards Institute, and many countries applies the fourth-root-of-2 principle, and the openings are fully compatible with the Tyler standard scale even though the sieve designations may vary (Table 19-6).

TABLE 19-5 Types of Screening Operations

Operation and description	Type of screen commonly employed
Scalping—Strictly, the removing of a small amount of oversize from a feed which is predominantly fines. Typically, the removal of oversize from a feed with approximately a maximum of 5% oversize and a minimum of 50% half-size.	Coarse (grizzly); fine, same as fine separation; ultrafine, same as ultrafine separation.
Separation (coarse)—Making a size separation at 4 mesh and larger.	Vibrating screen, horizontal or inclined.
Separation (fine)—Making a size separation smaller than 4 mesh and larger than 48 mesh.	Vibrating screen, horizontal or inclined; high-speed low-amplitude vibrating screens; sifter screens; static sieves; centrifugal screens.
Separation (ultrafine)—Making a size separation smaller than 48 mesh.	High-speed low-amplitude vibrating screen; sifter screens; static sieves; centrifugal screens.
Dewatering—Removal of free water from a solids-water mixture. Generally limited to 4 mesh and above.	Horizontal vibrating screen; inclined vibrating screens (about 10°); centrifugal screen.
Trash removal—Removal of extraneous foreign matter from a processed material. Essentially a form of scalping operation. Type of screen employed will depend on size range of processed material—coarse, fine, or ultrafine.	Vibrating screen, horizontal or inclined; sifter screens; static sieves; centrifugal screen.
Other applications: Desliming—Removal of extremely fine particles from a wet material by passing it over a screening surface. *Conveying*—In some instances transport of the material may be as important as the operation. *Media recovery*—A combination washing and dewatering operation.	Vibrating screens, inclined and horizontal; oscillating screens; centrifugal screens.

Testing Sieves Many product specifications require size of material in terms of given percentages passing or retained on specified test sieves. Test sieves are also generally used to determine the efficiency of screening devices and the work of crushing and grinding machinery.

It is essential that standard sieves, with standard-size openings be used for sieve analyses. The time of screening and the method of agitating the material on the sieve should also be standard, and in many industries the practice of specifying the test-sieve designation and the time and method of sieving is followed. An excellent overview of the theory and use of standard testing sieves is given in the *Testing Sieve Handbook*, No. 53, published by W. S. Tyler, Inc., Mentor, Ohio.

U.S. Sieve Series The American Society for Testing and Materials in cooperation with the National Bureau of Standards and the American National Standards Institute has further refined the U.S. sieve series, combining the former coarse and fine series into a single series series with a fourth-root-of-2 ratio (Table 19-6). The openings in the individual sieves have remained unchanged except for minor adjustments in sieves coarser than 0.00673 m (6.73 mm). In the revised series, sieves 1 mm and coarser are identified by opening in millimeters, and those finer than 1 mm by their openings in microns.

Tyler Standard Sieve Series Many users base their tests on Tyler standard testing sieves (Table 19-6). The only difference between the U.S. sieves and the Tyler screen scale sieves is the identification method. Tyler screen scale sieves are identified by nominal meshes per linear inch while the U.S. sieves are identified by millimeters or micrometers or by an arbitrary number which does not necessarily mean the mesh count. The Tyler standard sieve scale series has as its base a 200-mesh screen in which the opening is 7.37×10^{-5} m (0.0029 in) and the wire diameter 5.35×10^{-5} m (0.0021 in).

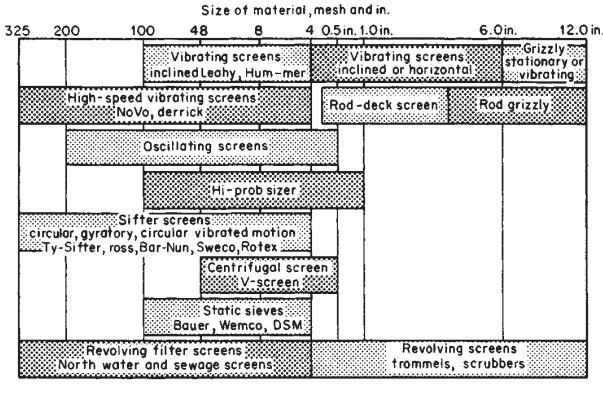


FIG. 19-14 Range of separations that can be obtained with various kinds of screens. To convert inches to meters, multiply by 0.0254. [*Matthews,* Chem. Eng. *(Feb. 15, 1971).*]

International Test Sieve Series The International Organization for Standardization (ISO) has been intensifying its efforts to establish an international test sieve series. At a meeting held at The Hague in October 1959, the ISO provisionally recommended for adoption as an international standard 19 sieves as shown by the data in Table 19-6. These sieves correspond to every alternating sieve in the fourth-root-of-2 U.S. sieve series from 0.022-m (8/8-in) opening to 325 mesh. The ISO has prepared a manual of sieving procedures that is available through the American Society for Testing and Materials.

The Ro-Tap testing sieve shaker (Fig. 19-15) manufactured by the W. S. Tyler, Inc., is the standard machine for automatically carrying out sieve-test procedures with accuracy and dependability. This device is built to hold a series of 0.203-m- (8-in-) diameter Tyler standard scale testing sieves and imparts to the sieves both a circular and a tapping motion. In effect, it reproduces the circular and tapping motion given testing sieves in hand sieving but does it with a uniform mechanical action. An important feature of the Ro-Tap is that both speed and stroke are fixed and not adjustable. This ensures the comparability between a number of sieve tests not only in a manufacturer's plant but between tests of a supplier and a customer.

The Ro-Tap is equipped to handle from 1 to 13 sieves at a time and is equipped with a timer that automatically terminates the test after any predetermined time.

Another mechanical shaker is the End-Shak, made by the Newark Wire Cloth Co. Sieves used are Newark test sieves, made to conform with the U.S. standard series.

A number of less expensive sieve shakers are on the market, such as the Dynamic, by Soiltest Inc., Chicago; the Cenco-Meinzer, by Central Scientific Co., Chicago; the Tyler portable, by W. S. Tyler, Inc., Mentor, Ohio; and also a number of electromagnetic vibratory shakers. The latter should be used only when strict comparability with other tests is not required, since it is difficult to be sure that identical intensity of vibration was present in the tests being compared.

Equipment Screening machines may be divided into five main classes: grizzlies, revolving screens, shaking screens, vibrating screens, and oscillating screens. Grizzlies are used primarily for scalping at 0.05 m (2 in) and coarser, while revolving screens and shaking screens are generally used for separations above 0.013 m (½ in). Vibrating screens cover this coarse range and also down into the fine meshes. Oscillating screens are confined in general to the finer meshes below 4 mesh.

Grizzly Screens These consist of a set of parallel bars held apart by spacers at some predetermined opening. Bars are frequently made of manganese steel to reduce wear. A grizzly is widely used before a primary crusher in rock- or ore-crushing plants to remove the fines before the ore or rock enters the crusher. It can be a stationary set of bars or a vibrating screen.

Stationary grizzlies. These are the simplest of all separating devices and the least expensive to install and maintain. They are normally lim-

TABLE 19-6 U.S. Sieve Series and Tyler Equivalents
(ASTM—E-11-61)

Sieve designation		Sieve opening		Nominal wire diam.		
Standard	Alternate	mm	in (approx. equiva-lents)	mm	in (approx. equiva-lents)	Tyler equivalent designation
107.6 mm	4.24 in	107.6	4.24	6.40	0.2520	
101.6 mm	4 in†	101.6	4.00	6.30	.2480	
90.5 mm	3½ in	90.5	3.50	6.08	.2394	
76.1 mm	3 in	76.1	3.00	5.80	.2283	
64.0 mm	2½ in	64.0	2.50	5.50	.2165	
53.8 mm	2.12 in	53.8	2.12	5.15	.2028	
50.8 mm	2 in†	50.8	2.00	5.05	.1988	
45.3 mm	1¾ in	45.3	1.75	4.85	.1909	
38.1 mm	1½ in	38.1	1.50	4.59	.1807	
32.0 mm	1¼ in	32.0	1.25	4.23	.1665	
26.9 mm	1.06 in	26.9	1.06	3.90	.1535	1.050 in
25.4 mm	1 in†	25.4	1.00	3.80	.1496	
22.6 mm*	⅞ in	22.6	0.875	3.50	.1378	0.883 in
19.0 mm	¾ in	19.0	.750	3.30	.1299	.742 in
16.0 mm*	⅝ in	16.0	.625	3.00	.1181	.624 in
13.5 mm	0.530 in	13.5	.530	2.75	.1083	.525 in
12.7 mm	½ in†	12.7	.500	2.67	.1051	
11.2 mm*	7/16 in	11.2	.438	2.45	.0965	.441 in
9.51 mm	⅜ in	9.51	.375	2.27	.0894	.371 in
8.00 mm*	5/16 in	8.00	.312	2.07	.0815	2½ mesh
6.73 mm	0.265 in	6.73	.265	1.87	.0736	3 mesh
6.35 mm	¼ in†	6.35	.250	1.82	.0717	
5.66 mm*	No. 3½	5.66	.223	1.68	.0661	3½ mesh
4.76 mm	No. 4	4.76	.187	1.54	.0606	4 mesh
4.00 mm*	No. 5	4.00	.157	1.37	.0539	5 mesh
3.36 mm	No. 6	3.36	.132	1.23	.0484	6 mesh
2.83 mm*	No. 7	2.83	.111	1.10	.0430	7 mesh
2.38 mm	No. 8	2.38	.0937	1.00	.0394	8 mesh
2.00 mm*	No. 10	2.00	.0787	0.900	.0354	9 mesh
1.68 mm	No. 12	1.68	.0661	.810	.0319	10 mesh
1.41 mm*	No. 14	1.41	.0555	.725	.0285	12 mesh
1.19 mm	No. 16	1.19	.0469	.650	.0256	14 mesh
1.00 mm*	No. 18	1.00	.0394	.580	.0228	16 mesh
841 micron	No. 20	0.841	.0331	.510	.0201	20 mesh
707 micron*	No. 25	.707	.0278	.450	.0177	24 mesh
595 micron	No. 30	.595	.0234	.390	.0154	28 mesh
500 micron*	No. 35	.500	.0197	.340	.0134	32 mesh
420 micron	No. 40	.420	.0165	.290	.0114	35 mesh
354 micron*	No. 45	.354	.0139	.247	.0097	42 mesh
297 micron	No. 50	.297	.0117	.215	.0085	48 mesh
250 micron*	No. 60	.250	.0098	.180	.0071	60 mesh
210 micron	No. 70	.210	.0083	.152	.0060	65 mesh
177 micron*	No. 80	.177	.0070	.131	.0052	80 mesh
149 micron	No. 100	.149	.0059	.110	.0043	100 mesh
125 micron*	No. 120	.125	.0049	.091	.0036	115 mesh
105 micron	No. 140	.105	.0041	.076	.0030	150 mesh
88 micron*	No. 170	.088	.0035	.064	.0025	170 mesh
74 micron	No. 200	.074	.0029	.053	.0021	200 mesh
63 micron*	No. 230	.063	.0025	.044	.0017	250 mesh
53 micron	No. 270	.053	.0021	.037	.0015	270 mesh
44 micron*	No. 325	.044	.0017	.030	.0012	325 mesh
37 micron	No. 400	.037	.0015	.025	.0010	400 mesh

*These sieves correspond to those proposed as an international (I.S.O.) standard. It is recommended that wherever possible these sieves be included in all sieve analysis data or reports intended for international publication.

†These sieves are not in the fourth-root-of-2 series, but they have been included because they are in common usage.

ited to the scalping or rough screening of dry material at 0.05 m (2 in) and coarser and are not satisfactory for moist and sticky material. The slope, or angle with the horizontal, will vary between 20 and 50°. Stationary grizzlies require no power and little maintenance. It is, of course, difficult to change the opening between the bars, and the separation may not be sufficiently complete.

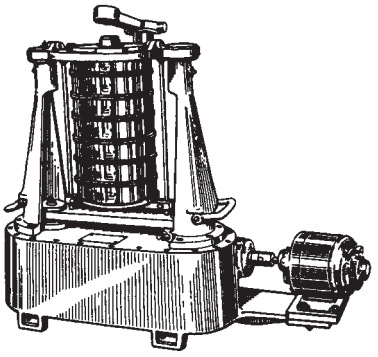


FIG. 19-15 Ro-Tap testing sieve shaker. (*W. S. Tyler, Inc.*)

Flat grizzlies. These, in which the parallel bars are in a horizontal plane, are used on tops of ore and coal bins and under unloading trestles. This type of grizzly is used to retain occasional pieces too large for the following plant equipment. These lumps must then be broken up or removed manually.

Vibrating grizzlies. These are simply bar grizzlies mounted on eccentrics so that the entire assembly is given a back-and-forth movement or a positive circle throw. These are made by companies such as Allis-Chalmers, Hewitt Robins, Nordberg, Link-Belt, Simplicity, and Tyler.

Revolving Screens Revolving screens, or trommel screens, once widely used, are being largely replaced by vibrating screens. They consist of a cylindrical frame surrounded by wire cloth or perforated plate, open at both ends, and inclined at a slight angle. The material to be screened is delivered at the upper end, and the oversize is discharged at the lower end. The desired product falls through the wire-cloth openings. The screens revolve at relatively low speeds of 15 to 20 r/min. Their capacity is not great, and efficiency is relatively low.

Mechanical Shaking Screens These screens consist of a rectangular frame which holds wire cloth or perforated plate and is slightly inclined and suspended by loose rods or cables or supported from a base frame by flexible flat springs. The frame is driven with a reciprocating motion. The material to be screened is fed at the upper end and is advanced by the forward stroke of the screen while the finer particles pass through the openings. In many screening operations such devices have given way to vibrating screens.

Shaking screens, such as the mechanical-conveyor type made by Syntron Co., may be used for both screening and conveying.

The advantages of this type are low headroom and low power requirement. The disadvantages are the high cost of maintenance of the screen and the supporting structure owing to vibration and low capacity compared with inclined high-speed vibrating screens.

Vibrating Screens These screens are used as standard practice when large capacity and high efficiency are desired. The capacity, especially in the finer sizes, is so much greater than that of any of the other screens that they have practically replaced all other types when efficiency of the screen is an important factor. Advantages include accuracy of sizing, increased capacity per unit area, low maintenance cost per ton of material handled, and a saving in installation space and weight.

There are a great number of vibrating screens on the market, but basically they can be divided into two main classes: (1) mechanically vibrated screens and (2) electrically vibrated screens.

Mechanically Vibrated Screens The most versatile vibration for medium to coarse sizing is generally conceded to be the vertical circle produced by an eccentric or unbalanced shaft, but other types of vibration may be more suitable for certain screening operations, particularly in the finer sizes. One well-known *four-bearing mechanically vibrated screen,* installed in an inclined position, is the Ty-Rock (Fig. 19-16). This is a balanced circle-throw machine mounted on a base frame, having a full-floating body mounted on shear rubber mounting units which absorb the shocks of heavy material and allow the shaft to revolve around its own natural center of rotation.

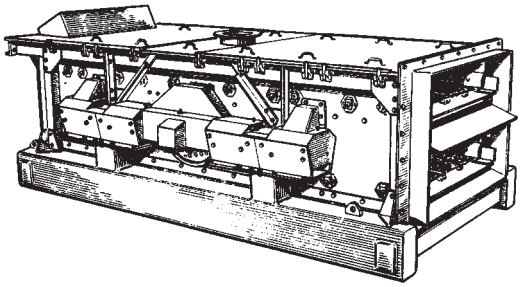


FIG. 19-16 Ty-Rock screen with air-seal enclosure. (*W. S. Tyler, Inc.*)

Two-bearing screens, of which there are many types, have the same screen body as the four-bearing type but without the two outer bearings and the base frame. The gyrating motion is caused by eccentric weights on the shaft, and the screen itself is supported by overhead cables or springs on the floor.

Screening machines actuated by rotating unbalanced weights have a symmetrical shaft through the screen body with an unbalanced flywheel on each end. Counterweights on each flywheel, which may be moved in relation to the shaft, permit adjustment of the amplitude of vibration. On some makes of machines the complete shaft assembly is contained in a unit bolted to the top of the screen body.

The horizontal-type screen is actuated by an enclosed mechanism consisting of off-center weights geared together on short horizontal shafts. The mechanism is usually mounted between the side plates and above the screen body (Fig. 19-17).

Electrically Vibrated Screens These screens are particularly useful in the chemical industry. They handle very successfully many light, fine, dry materials and metal powders from approximately 4 mesh to as fine as 325 mesh. Most of these screens have an intense, high-speed (25 to 120 vibrations/s) low-amplitude vibration supplied by means of an electromagnet.

Typical of these is the Hum-mer screen used throughout the chemical industry. Figure 19-18 shows one used throughout the fertilizer industry for handling mixed chemical fertilizers.

Oscillating Screens These screens are characterized by low-speed oscillations [5 to 7 oscillations per second (300 to 400 r/min)] in a plane essentially parallel to the screen cloth.

Screens in this group are usually used from 0.013 m (½ in) to 60 mesh. Some light free-flowing materials, however, can be separated at 200 to 300 mesh. Silk cloths are often used.

Reciprocating Screens These screens have many applications in chemical work. An eccentric under the screen supplies oscillation, ranging from gyratory [about 0.05-m (2-in) diameter] at the feed end to reciprocating motion at the discharge end. Frequency is 8 to 10 oscillations per second (500 to 600 r/min), and since the screen is inclined about 5°, a secondary high-amplitude normal vibration of about 0.0025 m (1/10 in) is also set up. Further vibration is caused by balls bouncing against the lower surface of the screen cloth.

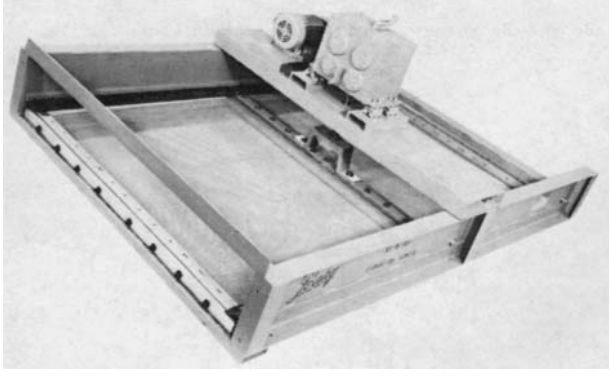


FIG. 19-17 Mechanically vibrated horizontal screen. (*Courtesy of Deister Concentrator Company, Inc.*)

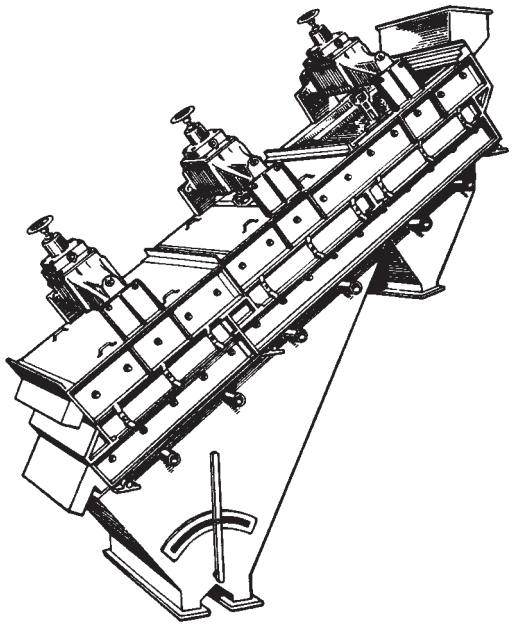


FIG. 19-18 Type 38 Hum-mer screen. (*W. S. Tyler, Inc.*)

These screens are used extensively in the United States and are standard equipment in many chemical and processing plants for handling fine separations even down to 300 mesh. They are used to handle a variety of chemicals, usually dry, light, or bulky materials, light metal powders, powdered foods, and granular materials. They are not designed for handling heavy tonnages of materials like rock or gravel. Machines of this type are exemplified by Fig. 19-19.

Gyratory Screens These are boxlike machines, either round or square, with a series of screen cloths nested atop one another. Oscillation, supplied by eccentrics or counterweights, is in a circular or near-circular orbit. In some machines a supplementary whipping action is set up. Most gyratory screens have an auxiliary vibration caused by balls bouncing against the lower surface of the screen cloth. A typical machine is shown in Fig. 19-20. Machines of this type are operated con-

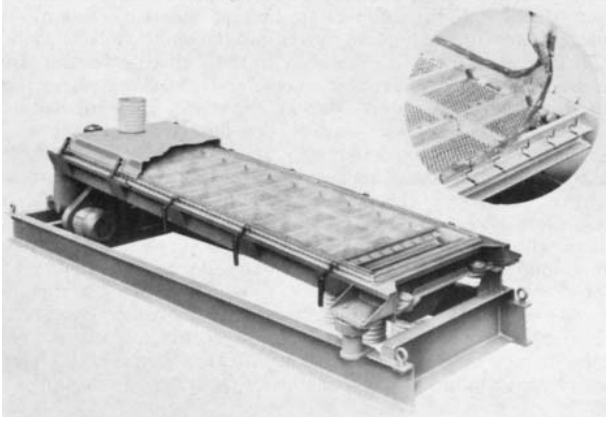


FIG. 19-19 Reciprocating screen. (*Courtesy of Rotex Corp.*)

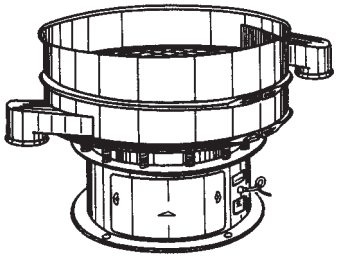


FIG. 19-20 Vibro-energy screen. (*Southwestern Engineering Company.*)

tinuously and can be located in line in pneumatic conveying systems as scalping screens. The size ranges from 0.6 to 1.5 m (24 to 60 in).

Gyratory Riddles These screens are driven in an oscillating path by a motor attached to the support shaft of the screen. The gyratory riddle is the least expensive screen on the market and is intended normally for batch screening.

Screen Surfaces The selection of the proper screening surface is very important, and the opening, wire diameter, and open area should all be carefully considered. The four general types of screening surfaces are woven-wire cloth, silk bolting cloth, punched plate, and bar or rod screens.

Woven-Wire Cloth This type has by far the greatest selection as to screen opening, wire diameter, and percentage of open area. Thousands of specifications are available from over 0.10 m (4 in) clear opening to 500 mesh. Woven-wire screens are obtainable in a variety of metals and alloys. Steel and high-carbon steel are generally favored for the coarser openings because of their abrasion-resistant qualities, and other materials, such as phosphor bronze, Monel, and stainless steel, are used for their corrosion-resisting or noncontamination qualities.

Square-mesh cloth is the conventional type of screen cloth, but there are many types of cloth with an oblong weave. This latter construction provides greater open area and capacity and in addition makes it possible to use stronger wire for the same size of screen opening and for the same percentage of open area.

In choosing a wire-cloth specification there must be a compromise between sharpness of separation, capacity, freedom from blinding, and life of the wire cloth. The square-mesh cloth will give the closest control of the maximum size particle in the undersize material; but the effective size of the openings will be reduced, because of the foreshortening when used at an angle of inclination, with consequent reduction in capacity. It should be realized that it is often necessary to use a cloth specification with an aperture larger than the smallest-size material acceptable in the oversize in order to ensure thorough removal of the undersize. A screen with a rectangular opening will increase the capacity with but little loss of sharpness when handling rounded or cubical grains. Slabby or flat material may also be handled on rectangular-opening cloth if the final-product specification will allow in the undersize a certain percentage of flat pieces having one dimension greater than the specified square-opening sieve. In other words pieces that might fall through a rectangular cloth and be allowed in the product might not go through the limiting square-mesh sieve on which the specification is based. If the through product is to be further ground or processed, a small amount of this material will not be objectionable.

Screen-cloth specifications having a relatively large length-to-width ratio are desirable when moisture or sticky material tends to cause blinding with square or short rectangular openings.

The finer the diameter of the wire from which a given specification is woven, the greater will be its screening capacity, although its screening life will be shorter. Since production capacity is generally more important than screen-surface cost, care should be taken to avoid using too heavy a specification which might restrict the capacity of the screening unit on which it is used and thus create a bottleneck in the flow.

Catalogs of wire-cloth manufacturers should be consulted for further study of the different types of wire-cloth specifications.

Silk Bolting Cloth This material originated in Switzerland and is generally woven from twisted multistrand-natural silk. The system of numbers and grades for both bolting cloth and gritz gauze has been handed down from the original Swiss weavers. In recent years, nylon and similar synthetic materials woven largely from monofilaments have been introduced. The nylon grades are generally designated by their micrometer opening and are available in light, standard, and heavy weights.

Comparative Openings of Screening Cloths In screening any material, the size of the particles going through the screen is determined by the actual opening and not by the number of meshes per linear unit. As a rule, the lighter grades of wire-screen cloth, having greater percentages of open area, screen more freely and accurately and should be used whenever they will give satisfactory length of service. Tables of comparative openings are available for selecting a screen specification with a specific opening or for picking a specification having a heavier or lighter wire but the same opening.

Punched Plates These are available in a variety of perforations including round, square, hexagonal, and elongated openings. Punched metal will generally wear longer than wire cloth and has more rigidity, which is an advantage in certain applications. However, it usually does not give the capacity per unit area that wire cloth does and is generally heavier. Its use is normally limited to the coarser separations.

Bar Screens These screens are generally used in handling large and heavy pieces of material. They are formed from rails, rods, or bars, suitably shaped; made from rolled steel or castings; fixed in parallel position and held by crossbars and spacers. Bars, which taper in thickness from top to bottom and may also taper in width from one end to the other, are recommended because they tend to avoid blinding.

Rod decks, composed of spring-steel rods approximately 0.6 m (2 ft) long, sprung into position between molded-rubber blocks, and held in position by means of rubber spacers, are also available.

Probability Screening Principle Probability screening uses the fact that particles moving almost at right angles to a screening surface are not likely to pass through when the particle size is greater than about half of the distance between the screen elements. Screens utilizing the probability principle are manufacturing by Dutch State Mines (DSM), Bartles (CTS), and Morgensen. The last-named incorporates multiple decks. Higher throughput, longer screen life, and lower capital costs are claimed for these screening systems. The performance of several types of probability screens was reviewed by Moir (op cit.).

Factors in Selecting Screening Equipment In attempting to pick a screening machine for a specific screening problem it should be emphasized that generalized formulas and charts used to predict screen capacity can give only an approximation because of the many variables which may affect performance. Screen consultants will readily admit that they must depend largely on laboratory tests and field experience. However, two governing factors bear mention: generally width of screen relates to capacity and length of screen relates to efficiency. Width is necessary to reduce the bed thickness to a practical maximum and length to allow the undersize to be removed without an inordinate amount of fines in the oversize. In attempting to choose a screening machine for a particular screening application the customer and manufacturer should consider the following: (1) Full description of material involved, including the name and type of material, bulk density, and physical characteristics such as hardness, particle shape, flow characteristics (free-flowing, sluggish, or sticky), percent of moisture and temperature. (2) Normal and maximum total rate of feed to screen. (3) Complete sieve analysis of screen feed, including maximum lump size, and sieve analysis of desired product. (4) Separation or separations required and the purpose of screening. Can slotted or rectangular openings be used in place of square openings? (5) Is screening to be accomplished dry or wet, and what amount of water is available? (6) Other important factors include method of delivering feed to the screen, open or closed circuit, open or enclosed screens, previous screening experience with the material, flow sheet or description of related equipment, operating hours per day, power available, and space limitations.

Variables in Screening Operations It will readily be seen that many variables in a screening operation can easily be changed in the

field, and practical operators will always be trying to improve their operations or adapt them to new products or processes. Capacity and efficiency in screening operations are closely related. Capacity may be large if low efficiency is not objectionable. Usually, as the tonnage to a screen is increased, efficiency is decreased.

Method of Feed The screening machine must be fed properly in order to obtain maximum capacity and efficiency. The feed should be spread evenly over the full width of the screen cloth and approach the screen surface in a direction parallel to the longitudinal axis of the screen and at as low a practical velocity as is possible.

Screening Surfaces It is generally agreed that the most efficient screening results when a series of single-deck screens is used. This is true because lower decks of multiple-deck screens are not fed so that their entire area is used and because each separation requires a different combination of angle, speed, and amplitude of vibration for maximum performance.

Angle of Slope The optimum slope of inclined vibrating screens is that which will handle the greatest volume of oversize and still remove the available undersize required by the standards of the particular operation. To separate a material into coarse and fine fractions, the bed thickness must be limited so that vibration can stratify the load and allow fines to work their way to the screen surface and pass through the opening. Increased slope naturally increases the rate of travel, and at a given rate it reduces the bed thickness.

In the oscillating screen the angle of inclination must be coordinated with the speed and stroke for best results.

Direction of Rotation In circle-throw screens somewhat greater efficiency can be obtained by counterflow rotation, that is, having the material move down the screen against the rotation. Screens rotating with the flow of material will handle greater tonnage and operate at a lower angle.

Vibration Amplitude and Frequency Speed and amplitude of vibration should be designed to convey the material properly and to prevent blinding of the cloth. They are somewhat dependent upon the size and weight of the material being handled and are related to the angle of installation and the type of screen surface. The object, of course, is to see that the feed is properly stratified for the most efficient separation.

Noise and Safety Noise is generated in screening due to the impact of the feed material on the screen surface. The drive mechanism also generates noise. Rubber and rubber bearings reduce substantially feed-impact noise with the added longer life of the decks. Noise from the drive mechanism is reduced by enclosing the mechanism in a box or by adding rubber linings to the side plates to dampen the noise.

Depending on the feed materials, the dust generated during operation may be hazardous because of possible emissions and toxicity. These hazards must be carefully evaluated before proper design of the facility and selecting the apparatus.

Performance Formulas

Screen Efficiency There is confusion concerning the meaning of screen efficiency, as a uniform method for figuring efficiency has never been established. A sound method of evaluating screen performance is given by W. S. Tyler, Inc., Mentor, Ohio, in its *Sieve Handbook*, no. 53. In this formula, when material put through the screen is the desired product, "efficiency" is the ratio of the amount of undersize obtained to the amount of undersize in the feed.

$$E = (R \times d)/b \tag{19-5}$$

where E = efficiency, R = percent of fines through the screen, d = percent finer than the designated size in screen fines, and b = percent finer than the designated size in screen feed.

When the object is to recover an oversize product from the screen, efficiency may be expressed as a ratio of the amount of oversize obtained to the amount of true oversize:

$$E = (O \times c)/a \tag{19-6}$$

where O = percent of oversize over the screen, c = percent coarser than the designated size in screen oversize, and a = percent coarser than the designated size in screen feed.

Other formulas for the derivation of screen efficiency are used. Taggart (*Handbook of Mineral Dressing*) gives the formula

$$E = 100 \times \frac{100(e - v)}{e(100 - v)}$$

where E is the efficiency, e is the percentage of undersize in the feed, and v is the percentage of undersize in the screen oversize.

Graphical methods of evaluating efficiency, using sieve analyses, are also employed and are recommended when serious research on screening is done.

Estimating Screen Capacity Various methods of predicting screening capacity have been proposed, and each has its limitations. The throughflow method of Matthews uses the following equation:

$$A = 0.4C_t/C_u F_{oa} F_s \tag{19-7}$$

where A = screen area
C_t = throughflow rate
C_u = unit capacity
F_{oa} = open-area factor
F_s = slotted-area factor

The unit capacity C_u can be determined from Fig. 19-21. Figure 19-22 can be used to determine the open-area factor F_{oa}, and the slotted-opening factor F_s for various screen types is given in Table 19-7.

WET CLASSIFICATION

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Introduction Wet classification is defined here as that art of separating the solid particles in a mixture of solids and liquid into fractions according to particle size or density by methods other than screening. In general, the products resulting are (1) a partially drained fraction containing the coarse material (called the underflow) and (2) a fine fraction along with the remaining portion of the liquid medium (called the overflow).

The classifying operation is carried out in a pool of fluid pulp confined in a tank arranged to allow the coarse solids to settle out, whereupon they are removed by gravity, mechanical means, or induced pressure. Solids which do not settle report as overflow. Mesh of sepa-

TABLE 19-7 Slotted-Opening Factors

Screen type	Length-to-width ratio
Square and slightly rectangular openings	Less than 2
Rectangular openings	Equal to or greater than 2 but less than 4
Slotted openings	Equal to or greater than 4 but less than 25
Parallel-rod decks	Equal to or greater than 25

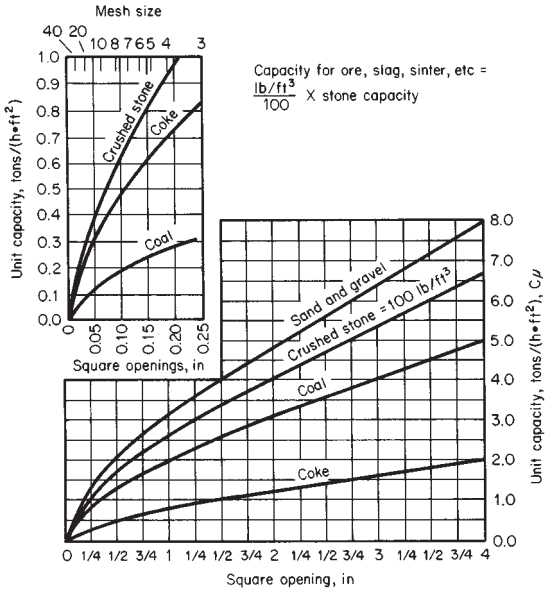


FIG. 19-21 Unit capacity (C_u) for square-opening screens. To convert inches to meters, multiply by 0.0254; to convert tons per hour-square foot to kilograms per second-square meter, multiply by 2.7182.

Aperture	Formula
Rectangular openings	$F_{oa} = \frac{a_1 a_2}{(a_1 + d_1)(a_2 + d_2)} \times 100$ F_{oa} is open area, %; d is diameter of wire, or horizontal width of bar (for plate), a is clear opening dimension (21-4)
Square openings Specified by opening size	$F_{oa} = 100 \left(\frac{a}{a+d}\right)^2$ $a_1 = a_2 = a$ $d_1 = d_2 = d$ (21-5)
Square openings Specified in mesh, m	$F_{oa} = 100\, a^2 m^2$ $m = \frac{1}{a+d}$ (21-6)
Parallel-rod decks	$F_{oa} = \frac{100a}{(a+d)}$ (21-7)
Special weaves	Assuming $a_3 = a_1$; $F_{oa} = 100 \left[\frac{a_1(a_2 + 2a_1)}{(a_2 + 2a_1 + 3d_2)(a_1 + d_1)}\right]$ (21-8)

FIG. 19-22 Open-area factor (F_{oa}) for flow-through screen-capacity calculation.

ration as used in this text is the screen size retaining 1½ percent of the overflow solids.

All wet classifiers depend on the difference in settling rate between coarse and fine or heavy- and light-specific gravity particles to be separated. Rates can be controlled to some extent by mild agitation, providing for hindered settling, and centrifugal force versus gravity in centrifuging types of units.

Several fundamental laws on classification are:

1. Coarse particles have a relatively faster settling velocity than fine particles of the same specific gravity.
2. Heavy-gravity particles have a relatively faster settling velocity than light-gravity particles of the same size. High solids concentration increases the viscosity and density of the fluid medium.
3. Settling rates of solid particles become progressively slower as the viscosity or density of the fluid medium increases.

a. There is a point (called critical dilution) where the lowering of density or viscosity by addition of more liquid creates a velocity effect which overcomes normal classification settling velocity, thereby coarsening the separation.

b. Conversely, at this point less liquid will cause a viscosity and buoyancy effect which will also coarsen the separation.

Typical problems to be solved by wet-classification means fall into several broad categories such as (1) to effect a simple sand-slime separation resulting in two products; (2) to effect a concentration of smaller heavy-gravity particles in a product containing larger light-gravity particles; (3) to obtain a washing effect by successive dewatering, repulping in weaker solution, and further dewatering; (4) to sort solids having a full range of screen sizes into a number of partials each having a short range of screen sizes; and (5) to achieve closed-circuit control of grinding mills.

Classification is by definition used preponderantly in the treatment of raw materials. However, these raw materials find their way into chemical processing per se and thus become of interest to the chemical engineer, particularly when the products to be treated react better when of a defined cleanliness, size, gravity, or moisture content.

Classifier types fall into two basic categories: (1) gravitational and (2) centrifugal classifiers. Gravitational classifiers can be subdivided into (1) sedimentation and (2) hydraulic classifiers. Furthermore each type falls into mechanical and nonmechanical types.

There are numerous machines and machine types to obtain a number of different particle-size classes from solids having a full range of sizes, and there is much overlapping in the possibilities. Usually, one type will provide optimum economy for the specific problem involved.

The quick reference Table 19-8 will help by way of rapid elimination of poor possibilities. Following that the brief comments and illustrations will help pinpoint most probable selections. Further study of the more elaborate data in the references and contact with the usual suppliers are recommended, as there are many possible modifications of equipment which can improve operating results from any type of machine finally selected.

Nonmechanical Classifiers

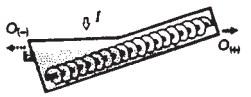
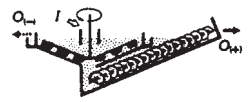
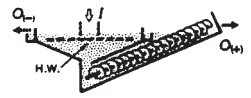
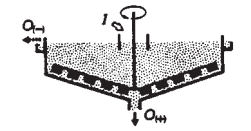
Cone Type Cone classifiers are one of the oldest types but are still used for relatively crude work because of low cost of installation. They are limited in diameter because of high headroom requirements caused by the ±60° sloping sides. Units are simple and are often fabricated locally with millwright ingenuity fashioning the apex opening arrangement for adjustment or control of the spigot coarse product. Operating attention is often necessary to a greater degree than for the more positive mechanical types. Cost figures are not available.

Hydrocyclone The wet cyclone classifier has rapidly achieved prominence since the 1950s and continues to gain popularity throughout chemical and ore-dressing industries. Standout virtues are its low capital cost and ability to make extremely fine separations by proper adjustment of design/operating condition. See Fig. 19-23.

In simplest terms the unit has a top cylindrical section and a lower conical section terminating in an apex opening, often adjustable. The unit operates under pressure induced by a static hydraulic head or by means of a pump forcing new feed into the cylindrical portion tangentially, thus producing centrifuging action and vortexing. The cover has a downward-extending pipe to cut the vortex and remove the overflow product called vortex finder. Coarse solids travel down the sides of the steeply sided cone section and are removed in a partially dewatered form at the apex.

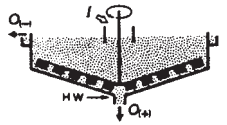
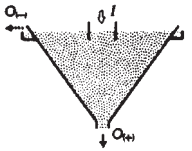
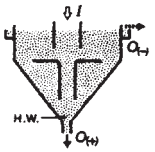
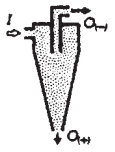
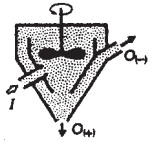
Hydrocyclones are available in numerous sizes and types ranging from pencil-sized 10-mm diameters of plastic to the 1.2-m (48-in) diameter of rubber-protected mild or stainless steel. Porcelain units 25 to 100 mm (1 to 4 in) in diameter are becoming popular, and in the 150-mm (6-in) size the starch industry has standardized on special molded nylon types. Small units for fine-size separations are usually manifolded in multiple units in parallel with up to 480 ten-mm

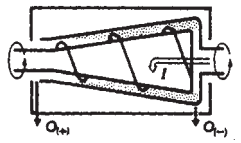
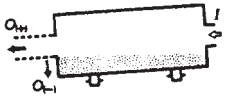
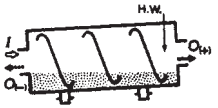
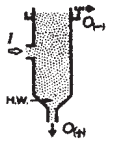
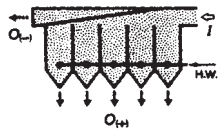
TABLE 19-8 The Major Types of Classifiers

Classifier	(Type*)	Description	Size (m) Width Diameter Max. length	Limiting size (max. feed size)	Feed rate (t/hr)	Vol. % solids Feed overflow underflow	Power (kW)	Suitability and applications
Sloping tank classifier (spiral, rake, drag) 	(M-S)	Classification occurs near deep end of sloping, elongated pool. Spiral, rake or drag mechanism lifts sands from pool.	0.3 to 7.0 2.4 (spiral) 14	1 mm to 45 μm (25 mm)	5 to 850	Not critical 2 to 20 45 to 65	0.4 to 110	Used for closed circuit grinding, washing and dewatering, deslimming; particularly where clean dry underflow is important. (Drag classifier sands not so clean.) In closed circuit grinding discharge mechanism (spirals especially) may give enough lift to eliminate pump.
Log washer 	(M-S)	Essentially a spiral classifier with paddles replacing the spiral.	0.8 to 2.6 0.6 to 1.1 4.6 to 11	(100 mm)	40 to 450		7.5 to 60	Used for rough separations such as removing trash, clay from sand. Also to remove or break down agglomerates.
Bowl classifier 	(M-S)	Extension of sloping tank classifiers, with settling occurring in large circular pool, which has rotating mechanism to scrape sands inwards (outwards in Bowl Desiltor) to discharge rake or spiral.	0.5 to 6.0 1.2 to 15 12	150 μm to 45 μm (12 mm)	5 to 225	Not critical 0.4 to 8 50 to 60 (15 to 25 in Bowl Desiltor)	Bowl: 0.75 to 7.5 Rake: 0.75 to 20	Used for closed circuit grinding (particularly regrind circuits) where clean underflow is necessary. Larger pool allows finer separations. Bowl Desiltor has larger pools (and capacities). Relatively expensive.
Hydraulic bowl classifier 	(M-F)	Basically a hydraulic bowl classifier. Vibrating plate replaces rotating mechanism in pool. Hydraulic water passes through perforations in plate and fluidizes sands.	–1.2 to 3.7 1.2 to 4.3 12	1 mm to 100 μm (12 mm)	5 to 225	Not critical 2 to 15 50 to 65	Vib: 2.2 to 7.5 Rake: 3.7 to 15	Gives very clean sands and has relatively low hydraulic water requirements (0.5 t/t underflow). One of the most efficient single-stage classifiers available for closed circuit grinding and washing. Relatively expensive.
Cylindrical tank classifier 	(M-S)	Effectively an overloaded thickener. Rotating rake feeds sands to central underflow.	— 3 to 45 —	150 μm to 45 μm (6 mm)	5 to 625	Not critical 0.4 to 8 15 to 25	0.75 to 11	Simple, but gives relatively inefficient separation. Used for primary dewatering where the separations involve large feed volumes, and underflow drainage is not critical.

*M: Mechanical transport of sands to discharge
N: Nonmechanical (gravity or pressure) discharge of underflow
S: Sedimentation classifier
F: Fluidized bed classifier
From Kelley, E. G. and D. J. Spottiswood, *Introduction to Mineral Processing*, John Wiley & Sons, New York, 1982, pp. 200–201, with permission.

TABLE 19-8 The Major Types of Classifiers (*Concluded*)

Classifier	(Type*)	Description	Size (m) Width Diameter Max. length	Limiting size (max. feed size)	Feed rate (t/hr)	Vol. % solids Feed overflow underflow	Power (kW)	Suitability and applications
Hydraulic cylindrical tank classifier 	(M-F)	Hydraulic form of overloaded thickener. Siphon-Sizer (N-F) uses siphon to discharge underflow instead of rotating rake.	— 1.0 to 40 —	1.4 mm to 45 μm (25 mm)	1 to 150	Not critical 0.4 to 15 20 to 35	0.75 to 11	Two-product device giving very clean underflow. Requires relatively little hydraulic water (2 t/t solids feed). Used for washing, desliming, and closed circuit grinding.
Cone classifier 	(N-S)	Similar to cylindrical tank classifier, except tank is conical to eliminate need for rake.	— 0.6 to 3.7 —	600 μm to 45 μm (6 mm)	2 to 100	Not critical 5 to 30 35 to 60	None	Low cost (simple enough to be made locally), and simplicity can justify relatively inefficient separation. Used for desliming and primary dewatering. Solids buildup can be a problem.
Hydraulic cone classifier 	(M-F)	Open cylindrical upper section with conical lower section containing slowly rotating mechanism.	— 0.6 to 1.6 —	400 μm to 100 μm (6 mm)	10 to 120	Not critical 2 to 15 30 to 50	3 to 7.5	Used primarily in closed circuit grinding to reclassify hydrocyclone underflow.
Hydrocyclone 	(N-S)	(Pumped) pressure feed generates centrifugal action to give high separating forces, and discharge.	— 0.01 to 1.2 —	300 μm to 5 μm (1400 μm to 45 μm)	to 20 m^3/min	4 to 35 2 to 15 30 to 50	35 to 400 kN/m^2 pressure head	Small cheap device, widely used for closed circuit grinding. Gives relatively efficient separations of fine particles in dilute suspensions.
Air separator 	(N-S)	Similar shape to hydrocyclone, but higher included angle. Internal impellor induces recycle within classifier.	— 0.5 to 7.5 —	2 mm to 38 μm	to 2100		4 to 500	Used where solids must be kept dry, such as cement grinding. Air classifiers may be integrated into grinding mill structure.

Solid bowl centrifuge 	(M-S)	Power generates high settling forces. Slurry centrifuged against rotating bowl, and removed by slower rotating helical screw conveyor within bowl.	— 0.3 to 1.4 1.8	74 μm to 1 μm (6 mm)	0.04 to 2.5 m^3/min	2 to 25 0.4 to 20 5 to 50	11 to 110	Relatively expensive, but high capacity for a given floor space; used for finer separations.
Scrubber 	(M-S)	Essentially a rotating drum mounted on slight incline.	— 1.5 to 3.5 3 to 10	(450 mm)	to 700		1 to 55	Similar applications to log washer, but lighter action. Tumbling (85% critical speed) provides attrition to remove clay from sand. Also removes trash.
Countercurrent classifier 	(M-F)	One form based on scrubber, another on spiral classifier. They have wash water added to flow essentially horizontally in opposite direction to underflow which is conveyed and *resuspended* by some form of spiral.	— 0.5 to 3.3 (spiral type) 12 (spiral type)	2 mm to 40 μm	3 to 600	Not critical 2 to 15 50 to 65	0.2 to 19	Very clean coarse product, but relatively low capacity for a given size.
Elutriator 	(N-F)	Basically a tube with hydraulic water fed near bottom to produce hindered settling. Underflow withdrawn through valve at base. Column may be filled with network to even out flow.	— 1.2 to 4.3 —	2.4 mm to 100 μm (7.5 mm)	4 to 120	15 to 35 0.4 to 5 20 to 35	0.75 for valves	Simple and relatively efficient separation. Normally a two-product device but may be operated in series to give a range of size fractions.
Pocket classifier 	(N-F)	A series of classification pockets, with decreasing quantities of hydraulic water in each, producing a range of product sizes.	0.5 to 6.0 — 12	2.4 mm to 100 μm (10 mm)	4 to 120	15 to 35 0.4 to 5 20 to 35		Efficient separations, but requires 3 t hydraulic water/t solids feed. Used to produce exceptionally clean underflow fractioned into narrow size ranges.

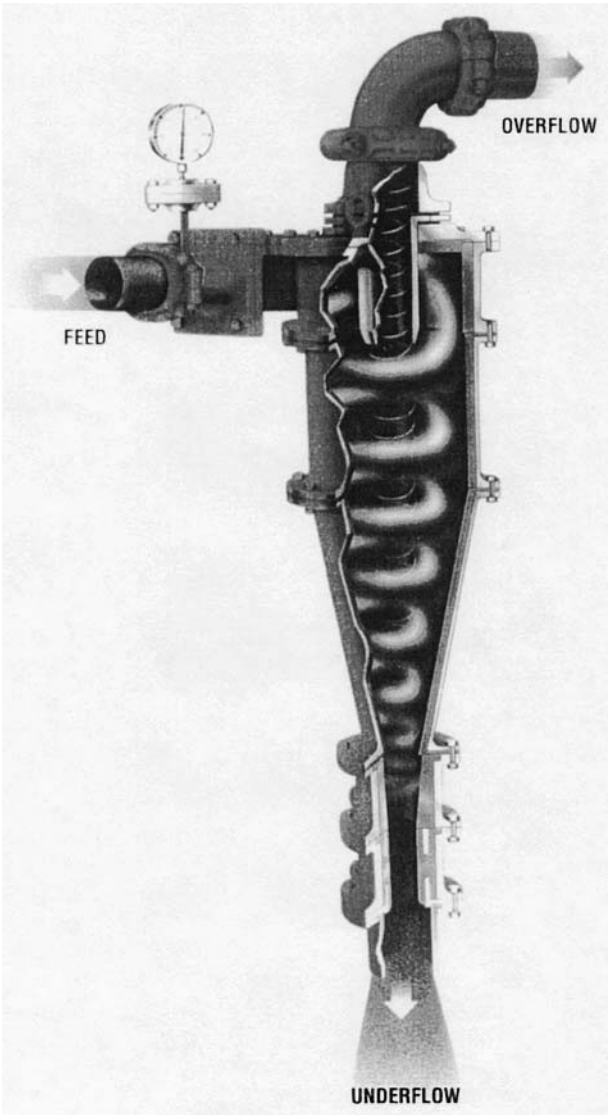


FIG. 19-23 Hydrocyclone. (*Courtesy Krebs Engineers.*)

cyclones in a single case. Larger sizes may be used singly or manifolded by outside piping.

The hydrocyclone has mostly replaced other classifiers in closed-circuit grinding.

Typical uses more in line with chemical applications are degritting milk of lime and of red mud in alumina production, removal of carbonaceous material in upgrading gypsum produced in making phosphoric acid, open-circuit washing of fine uranium pulps, classification of crystal magma such as lactose and sodium bisulfite, and classifying pigment and plastic beads into size ranges.

Mechanical Classifiers

Drag Classifiers Single endless-belt or chain suspensions with cross flights running in an inclined trough have long been used for draining and classifying. Many styles, sizes, and shapes have resulted from locally built units, and operating results on a scientific basis are meager. In general, they have served their purpose consistent with the type of engineering and cost included.

The Hardinge Overdrain* classifier is of the belt type, but it embodies the innovation of allowing entrapped water and slimes to escape through holes in the belt just uphill of the cross flights in an upward direction and thence flow down on top of the belt into the pool without again intermingling with the coarse product being advanced by the cross flights. Coarse product with lower moisture and fines content result from this action. Modern design and materials of construction permit sizes up to 3 m (10 ft) wide and 12.5 m (41 ft) long on steeper than average slopes and for very high tonnages.

Rake and Spiral Classifiers Rake-type classifiers such as the Dorr† classifier and spiral types such as the Akins‡ have been the workhorses for general-classification problems for half a century, and their names describe the mechanisms installed in sloping-bottom tanks. See Fig. 19-24. Mechanically the devices are powerfully built, and functionally they are versatile and flexible. They were the first classifiers used successfully for closed-circuit grinding. Separations as fine as 325 mesh can be accomplished at reduced tonnage rates.

Control of water into the classifiers is important since separation into fine and coarse products is made largely by the buoyancy, viscosity, and degree of agitation in the pool.

Both types of devices will produce rake products of consistent moisture content even with considerable variation in feed tonnage or volume.

Bowl Classifier The bowl classifier was developed to provide more separation area necessary for fine separations consistent with high tonnage. In essence a shallow bowl with revolving plows is superimposed over a rake or screw dewatering section. Feed enters at the center of the bowl, and fine solids overflow at the periphery. Coarse solids collected on the bowl bottom are raked to the center for discharge into the dewatering compartment below where wash water may be added for counterflow.

Hydrocyclones are rapidly taking over the functions formerly handled by bowl classifiers because of lower capital costs and floor-area requirements.

Bowl Desilter The bowl desilter provides for separation areas well beyond areas possible in bowl classifiers, in which larger sizes are limited by mechanical design. Its use is in operations involving large flow volumes and fine separations. Rake tonnages can be great or small with a dewatering compartment to suit the conditions.

In the bowl desilter the rotating blades in the bowl plow outward and discharge settled coarse material at the periphery, where it drops into the drainage compartment. This configuration does away with the long cantilevered rake construction necessary in bowl classifiers.

Widest application has been for the recovery of and drainage of very fine material overflowing coarser washing units in glass sand, concrete sand, coal, and limestone processing plants.

Hydroseparator The hydroseparator is merely a thickener-type machine receiving more flow than can be clarified in the area provided. Thus the overflow contains fine solids, and the greater the feed rate per unit of area the coarser the solids in the overflow.

Classification efficiency of the hydroseparator compares with that of the cone classifier and is appreciably lower than that obtained from mechanical or hydraulic units. The chief virtue of the hydroseparator is its ability to receive and slough off great quantities of water at low per-unit-volume cost.

Typical applications include primary dewatering of phosphate rock matrix and silica sand products following wet screening. In ore dressing it is used mainly to protect large-diameter thickeners by scalping out +65-mesh material.

Solid-Bowl Centrifuge The Bird solid-bowl centrifuge uses power instead of gravity and can develop centrifugal forces up to 1800 times the force of gravity. It is therefore a unique type in classification practice.

The unit consists essentially of two rotating elements, the outer being a solid-shell conical-shaped bowl and the inner comprising a helical-screw conveyor revolving at a speed slightly lower than that of the bowl. Raw feed slurry is delivered through a stationary feed pipe

* Trademark of Koppers Co., Inc.
† Trademark of Dorr-Oliver Inc.
‡ Trademark of Mine & Smelter.

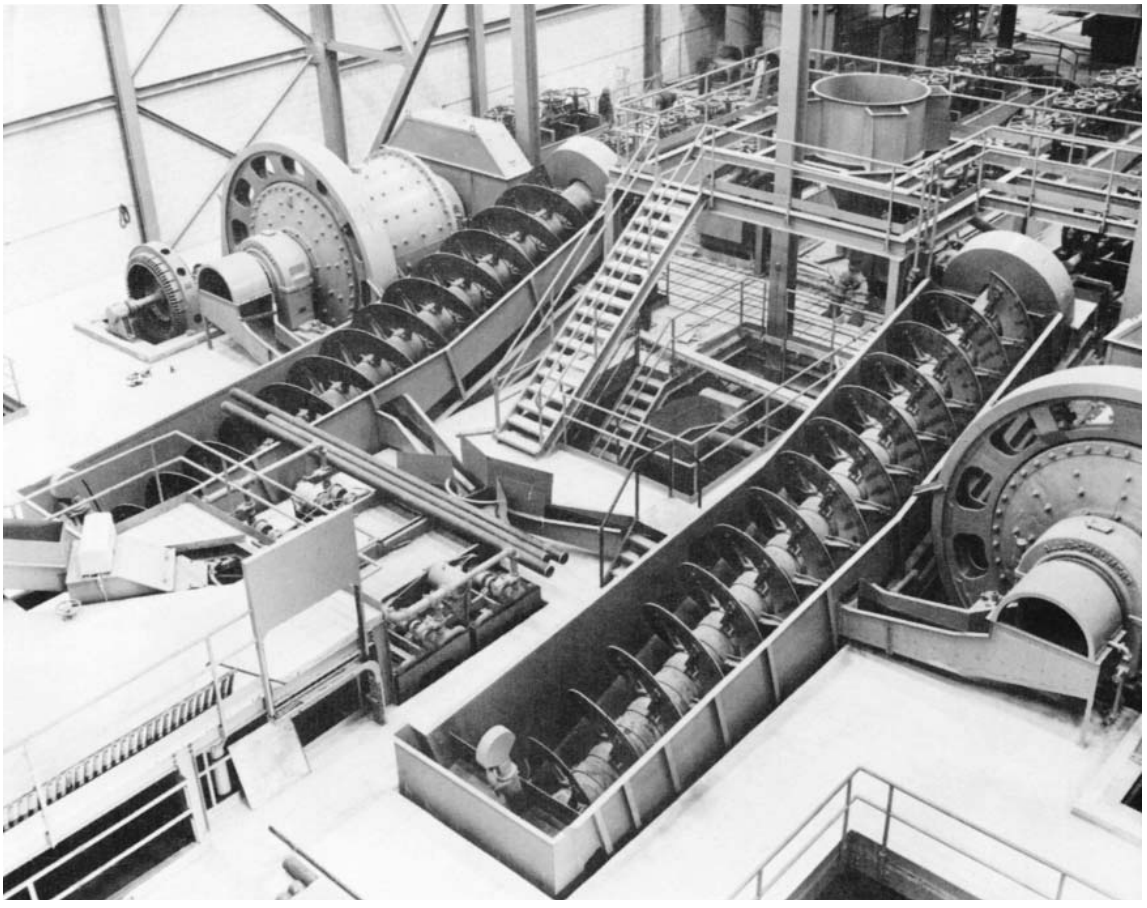


FIG. 19-24 Spiral type classifier. Wemco S-H 78-in classifiers in closed-circuit grinding operation at St. Joseph Lead Co., Indian Creek plant. (*Courtesy Wemco Div., Envirotech Corp.*)

to the conveyor, where, urged by centrifugal force, it is transferred to the revolving bowl. A circumferential classifying area is formed and contained at the larger diameter of the cone shell. The ports for oversize material are located closer to the axis of rotation than the ports for the overflow to effect a beach line and drainage.

Centrifugal force deposits the oversize particles against the bowl wall, from which they are conveyed by the helix. The overflow fractions flow around the helix to the liquid-discharge ports. Size of separation is controlled by feed rate and degree of centrifugal force.

Several prime features of this totally enclosed unit are its high capacity per unit of floor area, small volume of material in process, high degree of separation, and shear action for dispersion of solids. Typical applications are desliming to upgrade cement rock, sizing of abrasives, fractionating for reagent control, and classification of pigments.

Countercurrent Classifier The countercurrent classifier is an inclined, slowly rotating cylindrical drum with continuous spiral flights attached to the interior of the shell forming helical troughs. Direction of rotation is such that material in the troughs is impelled toward the higher end. The lower end of the shell is closed except for a central overflow opening. Attached to the upper end is a coarse solid dewatering elevator which rotates with the shell. Wash water introduced at the upper end drains from the lifting flights above the normal water level and progresses countercurrently to the sand toward the overflow.

Usual application is for sand-slime separations, washing and for closed construction restricting escape of heat and chemical fumes, easy start-up after shutdown, and general simplicity. Weights range from 500 to 55,000 kg (1100 to 120,000 lb).

Hydraulic Classifiers

Jet Sizer* and SuperSorter† The Jet Sizer and SuperSorter are multicompartment and, therefore, multiproduct classifiers operating on the basis of hindered settling. The classification pockets are arranged in series for throughflow with parallel pockets to take care of high tonnage size fractions. Each compartment is served with low-pressure hydraulic water.

Hydraulic classification ensures the highest separating efficiency obtainable by wet-classification means. The amount of hydraulic water is controlled so that in each succeeding compartment the coarsest particles are maintained in hindered-settling condition and the finer fractions pass along for similar treatment. Two compartments will normally capture 90 percent of a two-screen-size fraction. Spigot discharge is controlled by air-actuated valves in the Jet Sizer and motor-driven pincer-type valves in the SuperSorter. Solid fractions can be taken from single or combinations of compartments as desired.

Typical applications include careful sizing of silica-glass sand, washing phosphate rock, sizing of abrasives, smokeless powder, sodium aluminate, etc.

D-O SiphonSizer* The D-O SiphonSizer (Fig. 19-25) is a high-efficiency hydraulic classifier developed originally for the washing and sizing of phosphate rock. In ore-dressing work it is normally a two-product unit; but by use of an upper column sealed at the top and

* Trademark of Dorr-Oliver Inc.
† Trademark of Deister Concentrator Company, Inc.

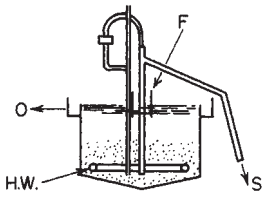


FIG. 19-25 D-O SiphonSizer.

open at the bottom, three products are possible: coarse, intermediate, and fine fractions.

Feed to be sized is put into hindered-settling condition by hydraulic water in quantity only sufficient to teeter the smallest particle wanted in the coarse product. The finer fractions report to the overflow or pass into the upper column for removal in a three-product unit.

Coarse solids are discharged by siphons extending to the bottom of the hindered-settling zone. Siphon control is obtained by a novel hydrostatically actuated valve which makes or breaks the siphon to flow only when the teeter zone is in correct condition. Discharge by an intermediate fraction from the upper column is by means of additional siphons. Hydraulic-water consumption is considerably lower than required for multipocket sizers.

SiphonSizers vary so widely in configuration that general cost data are not meaningful.

JIGGING

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Introduction A jig is a mechanical device used for separating materials of different specific gravities by the pulsation of a stream of liquid flowing through a bed of materials. The liquid pulsates, or "jigs" up and down, causing the heavy material to work down to the bottom of the bed and the lighter material to rise to the top. Each product is then drawn off separately.

Jigging is one of the oldest processes used for concentrating heavy mineral particles from the light. Jigging is best suited for coarse material that is unlocked in the size range 20 mesh and coarser and when there is a considerable difference between the effective specific gravity (sp gr mineral minus sp gr water) of the valuable and the waste material. Jigs are simple in operation. Water consumption is high, and the tailings losses on metallic ores are usually high. Also, because of the scarcity of still-available ore deposits having coarse mineralization, the jigs are used to a limited extent, mostly to treat iron ores, a few lead-zinc ores, and some heavy nonmetallic ores like barite and diamonds. Jigging is widely employed for the concentration of coal. Over 50 million tons of coal is concentrated by jigs annually in the United States. High-speed types of jigs are used for the recovery of fine-grained heavy minerals from placer deposits, gold, tin, and tungsten, and for recovering a portion of coarse metallic values liberated in ball-mill grinding circuits. Jigging has been superseded in many milling operations by the adoption of the dense-media process or by fine grinding followed by flotation.

Principles of Operation The principle of jig operation can easily be understood by taking a 10-mesh laboratory sieve, placing a 1 cm thick bed of a mixture of heavy and light particles, immersing the sieve in a bucket of water, and oscillating it up and down under water. The pulsations will dilate the bed of material and make the particles settle as the larger and denser particles forming the lower layers with the finer and lighter particles on the top.

The motion of the mixture of particles during jigging is modulated by the amplitude and frequency of jigging strokes and these strokes result in displacement of particle bed in a harmonic wave (Fig. 19-26*a*). During the pulsation stroke the original bed (Fig. 19-26*b*) dilates resulting in the bed as shown in Fig. 19-26*c.* During the suction stroke the bed of particles undergoes differential initial acceleration followed by hindered settling and consolidation trickling (Wills, op. cit.). It is found that the initial acceleration of the particles is independent of size and dependent only on the densities of the solids and fluid, thus causing the heavy particles to settle faster than the lighter as illustrated in Fig. 19-26*d.* The hindered settling on the other hand is controlled by both size and density of particles with smaller particles settling less and heavier settling more (Fig. 19-26*e*). Finally, during the consolidation trickling the bed begins to compact, the larger particles interlock and allow the smaller grains to move downwards (Fig. 19-26*f*).

Types of Jigs A jig is essentially an open tank filled with water and provided with a horizontal screen on the top and a *hutch* compartment fitted with a spigot (Fig. 19-27*a*). A layer of coarse, heavy particles, known as *ragging,* is placed on the top of the screen onto which the feed slurry is introduced. The feed moves over the ragging and the separation takes place as the bed is pulsated by a different mechanical device. The heavy particles are collected into the hutch compartment and removed through the spigot while the lighter particles are made to overflow from the top of the tank.

Several types of jigs are currently available with the main differences being in the pulsating mechanism and the stroke modification. Figures 19-27*b* through Fig. 19-27*e* illustrate four different designs that are commonly used. One of the earliest designs of jigs is the *Harz* and it uses reciprocating plunger with differential piston action (Fig. 19-27*b*). The Harz jig is commonly used in the treatment of gold, tungsten, and chromite ores. Remer jig (Fig. 19-27*c*) is an improvement over Harz by providing a driving mechanism that has two motions, a normal jig pulse of 80 to 120 strokes per minute on which imposed a fast pulse in the range of 200 to 300 per minute. This kind of jig is commonly used in concentrating such materials as iron and barite ores and in removing impurities such as wood, shale, and lignite from sand and gravel. In contrast, *Baum* and *Batac* jigs make use of air pulsations and are widely used in the coal-preparation industry to reduce the ash content of the run-of-mine coals. The standard Baum jig (Fig. 19-27*d*) operates by forcing air under pressure at about 17.2 kPa (2.5 lbf/in^2) into a large air chamber on one side of the jig vessel to pulsate the jig water which in turn pulsate the bed of particles fed onto the screen. Several design variations exist in the removal of lighter coal and heavier ash fractions (Green, op. cit). The Batac jig (Fig. 19-27*e*) is a modification of the Baum jig in that it employs multiple air chambers under the screen with electronic controls for air input and exhaust. This design is found to provide a uniform flow across the whole bed and a wide control of the speed and length of the jigging strokes. Batac jig is reported to treat both coarse- and fine-size coals satisfactorily (Chen, 1980) and has become an industry standard for coal cleaning (Zimmerman).

Jig Feed In coal washing jigging is practiced on unsized material as coarse as 175 mm (7 in). In metal-milling practice jigging is now seldom employed on material coarser than 20 mm (¾ in). Float-and-sink methods have largely superseded jigs as a way of concentrating metallic ores in the minus 75 to plus 10-mm (3 to plus ½-in) range. Shaking tables usually are considered more efficient than jigs for treating ores finer than 2 mm (10 mesh). Jigs are used in some plants to obtain flowsheet simplicity since they can handle a wide range of sizes. Jigs, except when extremely heavy minerals such as gold, galena, cassiterite, or tungsten minerals are treated, recover only a small percentage of the sizes finer than 65 mesh (¼ mm).

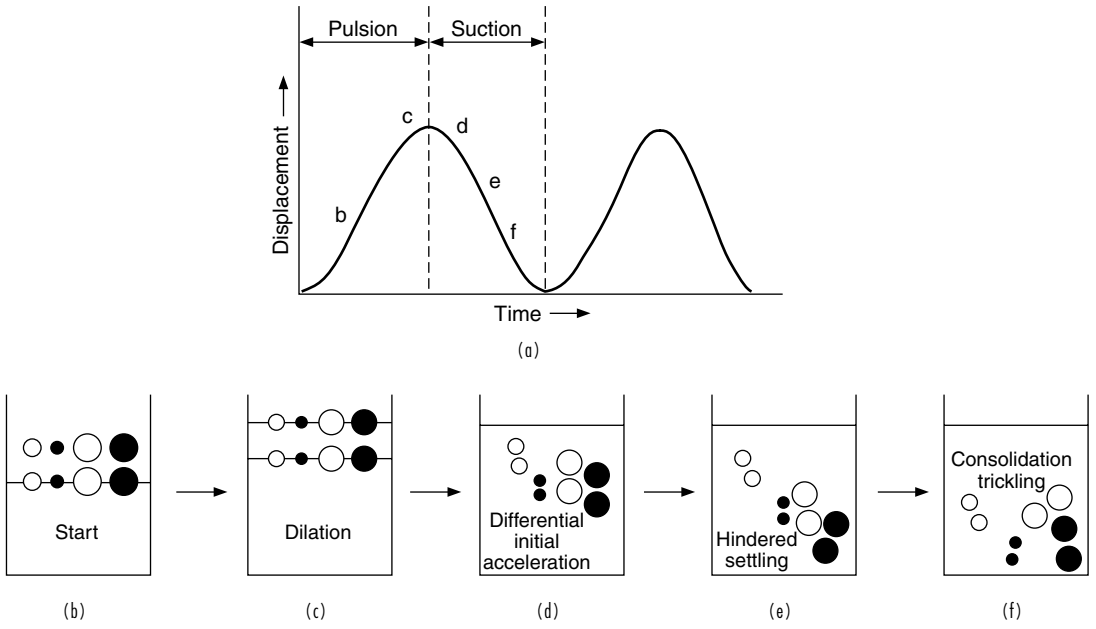


FIG. 19-26 Movement of particles in a jig. (*a*) Displacement of the bed as a function of time. (*b*) Starting position of particles. (*c*) After dilation. (*d*) After differential initial acceleration. (*e*) After hindered settling. (*f*) After consolidation trickling.

Capacity The Jeffrey-Baum will treat minus 100-mm (4-in) coal at the rate of 8 kg/(s·m^2) [3 tons/(h·ft^2)] of active screen area. For fine sizes capacity decreases. A standard 1.52- by 4.87-m (5- by 16-ft) Wemco-Remer jig will treat minus 9.5-mm (⅜-in) iron ore at the rate of 7.5 to 11.3 kg/s (30 to 45 tons/h). A Cooley jig, a variation of the Harz jig consisting of six compartments 1.07 by 1.22 m (42 by 48 in), will handle 6 to 7.5 kg/s (25 to 30 tons/h) of minus 19-mm (½-in) Mid-Continent zinc ore. The largest commercially available jig is the IHC Cleveland 25, a circular jig of 7.5-m (24.6-ft) diameter with a nominal capacity range of 30 to 60 kg/s (130 to 260 tons/h) of coal.

Power Requirements The power required in jigging depends on the screen area, the size of material treated, the percentage of opening in the jig screen, the depth of the bed, the length of stroke, and the choke frequency. The power required for plunger-type jigs treating 12.7-mm (½-in) material is about 7 W/m^2 (0.1 hp/ft^2) jig screen surface.

Water Consumption Jigs require much water. In most installations, the Harz-type jig uses 0.006 to 0.01 m^3 water/kg (1500 to 2500 gal/ton) material treated. Water requirements for treating minus 10-mm (⅜-in) iron ore in a Wemco-Remer rougher-cleaner jig circuit are approximately 0.005 m^3 water/kg (1200 gal/ton) of material processed.

TABLING

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Wet Tabling Tabling is a concentration process whereby a separation between two or more minerals is effected by flowing a pulp across a riffled plane surface inclined slightly from the horizontal, differentially shaken in the direction of the long axis, and washed with an even flow of water at right angles to the direction of motion. A separation between two or more minerals depends mainly on the difference in specific gravity between the minerals and to a lesser degree on the shape and size of the particles. The process is best suited for the concentration of ore and coal where there is a considerable difference between the effective specific gravity (sp gr mineral minus sp gr water) of the valuable and the waste material. Tables treat metallic ores effectively in the size range from 6 to 150 mesh but can be used to treat lighter materials such as coal of a considerably larger size.

Tabling is best suited for the treatment of material containing only one valuable mineral that is free at a granular size and when a considerable difference exists between the effective specific gravities of the mineral constituents. Flotation has been found to be best in treating complex ores containing several valuable minerals, those requiring fine grinding for liberation, and those having small gravity differentials.

The heaviest particles in a table feed are the least affected by the current of water washing down over the tables, and they collect in the riffles along which they move to the end of the table. The lighter materials ride above the heavy minerals and tend to be washed over the riffles to the low side of the table. Suitable launders are placed at the end of the low side of the table to catch the various products as they are discharged. These launders are provided with movable dividing devices to separate the concentrates from the middlings and the middlings from the tailings. It seldom is possible in tabling to make a sharp separation of the feed into a high-grade concentrate and a low-grade tailing with one pass. Some material of intermediate grade is almost invariably present as a band between these products, and it is customary to return such middlings either with or without additional grinding to the head of the circuit for retreatment. The amount of middling recirculated may amount to 25 percent of weight of the feed to the table.

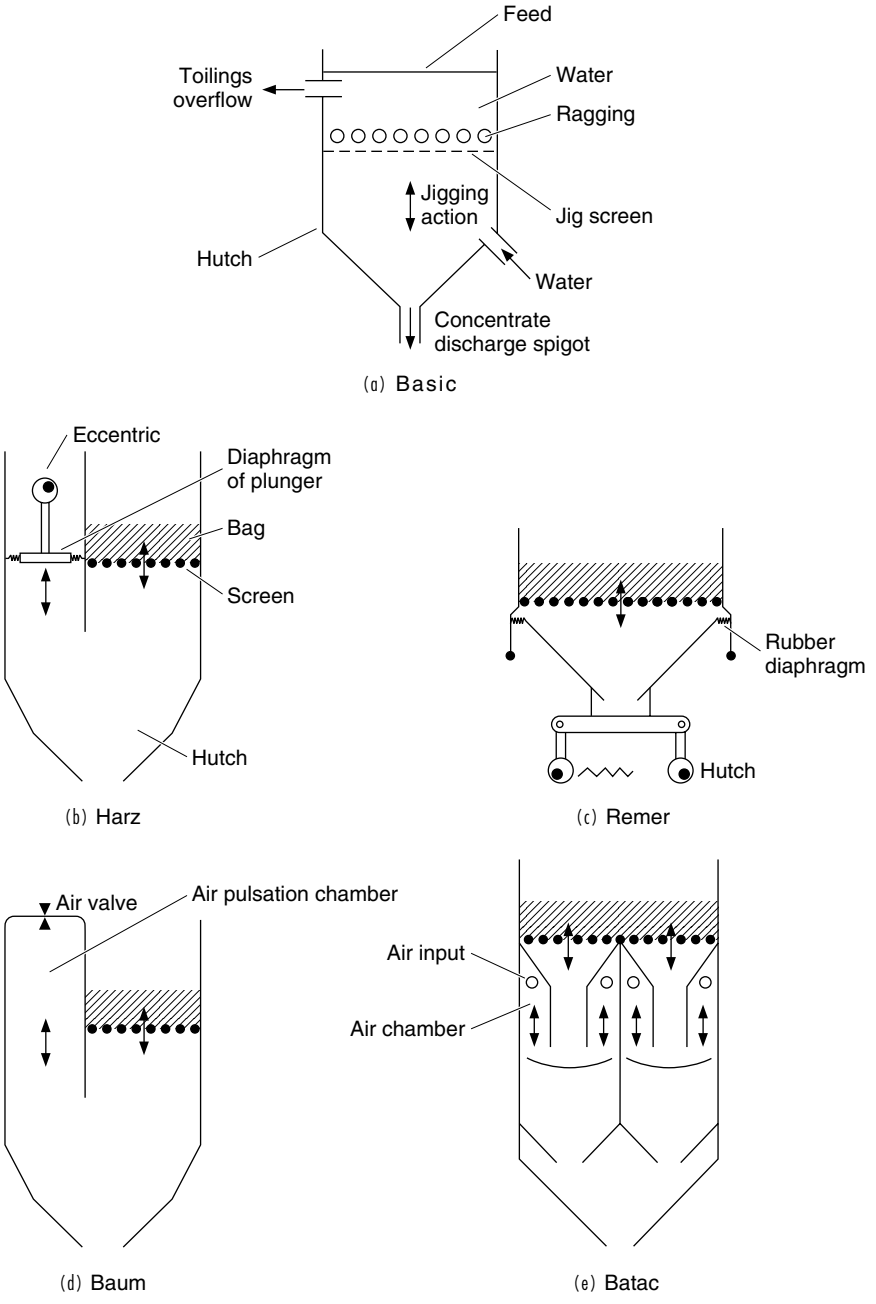


FIG. 19-27 Schematic diagrams of the jigs. (*a*) Basic, (*b*) Denver/Harz, (*c*) Remer, (*d*) Baum, and (*e*) Batac.

Tables usually are surfaced either with heavy battleship linoleum or with rubber. The riffles may be a clear grade of sugar pine or may be rubber strips. Such riffles usually taper from the feed end of the table to the discharge end. Almost all mill operators employ different styles of riffling table, which they believe best for their particular separations. The usual method of riffling is shown in Fig. 19-28.

If the object of tabling is to produce as clean a concentrate as possible, a diagonal area in the upper discharge side corner is left unriffled. This area is known as the cleaning deck. If the table is to be used in making only a rough concentrate and a finished tailing, the riffling is extended by many operators. Tables are provided with adjustable tilting devices so that the transverse slope may be varied. The head motion is such that the deck reverses its direction with a maximum velocity at one end and a minimum velocity at the other end of the stroke. It is the quickness of the return that causes the material to migrate toward the discharge end. The length of stroke may be adjusted. This will vary from 0.03 m (1¼ in) for coarse material to 0.01 m (½ in) for fines. Modern tables operate from 4 Hz (270 strokes/min) for coarse to 6 Hz (350 strokes/min) for fines.

Present table practice is to use multiple decks. Multiple-deck tables consisting of from two to three decks effect space saving proportionate to the number of decks employed. They also have the advantage in

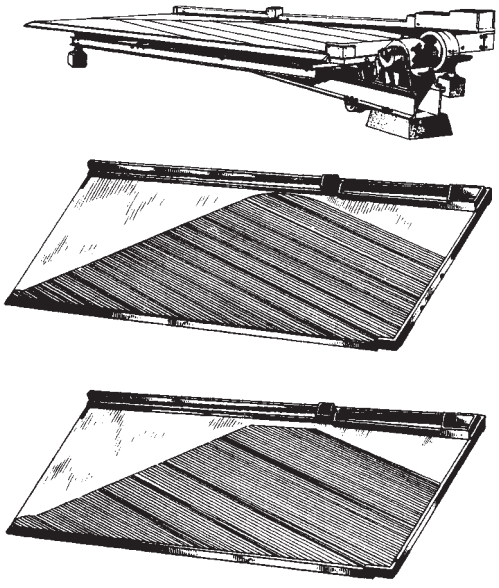


FIG. 19-28 Deister-Overstrom diagonal deck table. Center, diagonal deck with pool riffle system for sand; bottom, diagonal deck with pool riffle system for fine sand and slime.

that no heavy floor supports need be supplied since such tables are supported by suspended mountings. Multiple-deck installations reduce capital expenditures since a single motor and less piping and fewer launders are required than for a comparable number of single-deck installations. A two-deck configuration is shown in Fig. 19-29.

General information for standard-size tables operating on various-sized feeds is shown in Table 19-9. The No. 6 table of the Deister Concentrator Company, Fort Wayne, Indiana, has a diagonal deck approximately 1.83 m (6 ft) wide and 4.27 m (14 ft) long. The No. 7 table used primarily for coal work is approximately 2.44 m (8 ft) wide and 4.88 m (16 ft) long. The figures given apply to single-deck installations. In modern practice, each table, whether it be a single-deck or a multiple-deck installation, is driven by a single motor which is connected to the actuating mechanism by a V-belt drive. The installed

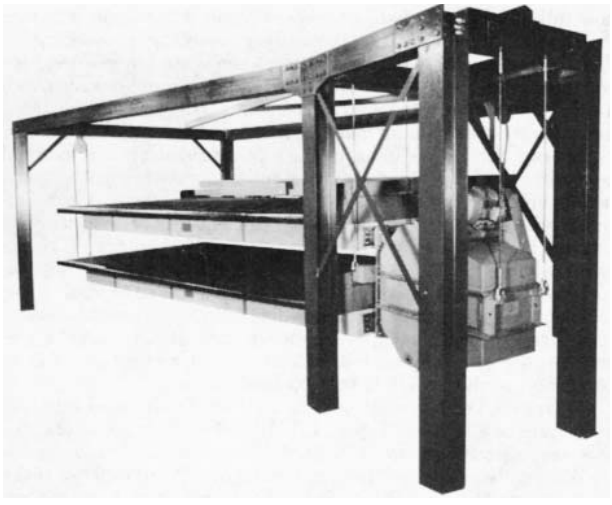


FIG. 19-29 Two-deck concentrating table. (*Courtesy Deister Concentrator Company, Inc.*)

horsepower for the large No. 7 deck is 1120 W (1.5 hp). A comparable figure for the smaller No. 6 deck is 746 W (1 hp) per deck. The actual power consumed in operation is somewhat less.

An essential factor for good table operation is that the rate of feed must be uniform, both as to tonnage and as to physical properties. No one factor will cause more trouble to the table operator than to have a surging feed. The feed to tables may be unsized, or it may be either screened or hydraulically classified. For treating fine coals a common procedure is to use hydrocyclones both to deslime the material and to give a cyclone underflow of about 40 percent solids, which constitutes the table feed.

Tabling is a relatively cheap operation. If the feed is uniform, one operator can take care of many tables. In a modern coal plant with multiple-deck tables, a single operator can handle the tabling of as much as 300 kg/s (1200 tons/h). In an ore-tabling plant such as a lead or zinc operation, a table operator can watch as many as 50 tables with a total capacity in the order of 50 kg/s (200 tons/h). Labor is the principal item of cost. Power requirements and maintenance are both low. The installed cost of a table including supports and launders is from $8000 to $15,000 per deck. In the past, one of the disadvantages of table installation was the relatively large floor space required for the tonnage treated. This disadvantage has now largely been overcome by the use of multiple-deck tables. Their main advantage is that, in the size range for which they are suited, tabling is a cheap and effective method of concentrating simple ores and coal.

Dry Tabling Tabling may be done dry as well as wet, and for such use tables of special design are used. The Sutton, Steele and Steele table is an example of this type of equipment. It has a shaking motion somewhat similar to that of a wet table, except that the direction of motion is inclined upward from the horizontal, and instead of water acting as the medium of distribution, a blast of air is driven through a perforated deck. The table has application when it is desirable to treat material dry, either because of water shortage or because it is undesirable to wet the materials. An advantage of this table is the ability to handle material coarser than that treated on most wet tables. Ores as coarse as 0.006 m (¼ in) and coal as coarse as 0.076 m (3 in) can be treated.

Close sizing is necessary to give good results, and until recently this has militated against adoption of the table for fine sizes, owing to the difficulties of screening most ores dry below about 40 mesh. The development of improved dry methods for sizing fine material by the use of various cyclonelike devices has tended to increase the use of this apparatus on finer sizes.

Dry tables are used commercially in the separation of many types of minerals. Their greatest use is in the treatment of coal, but ilmenite, various tungsten ores, and even copper ores are so treated. Another important use is the cleaning of industrial materials such as seeds, cork, bagasse, fiber, nuts, wood chips, and coffee. One interesting use is in the sorting of silicon carbide by grain shapes. Flat and splintery grains are removed from others of more nearly equal dimensions.

Agglomeration Tabling Agglomeration tabling is a process whereby selective flocculation or agglomeration of grains of one mineral in an aggregate is caused by the addition of an agglomerating agent in a conditioning cell or in the ball-mill circuit, the slurry containing the agglomerated grains then being fed across gravity tables. The larger size, the oil-filmed surface, and the feathery texture of the floccules cause them to be washed over the side of the table by the current of cross water, while the unflocculated discrete particles remain on the table and are carried off the end in the position followed normally by the concentrate in the usual table feed. An oiled particle will tend to ride on the surface of the water and thus is more readily carried across the side of the table than an unoiled particle. Agglomeration tabling has had more application in the concentration of phosphate minerals than in any other field, although successful tests have been run on limestone, potash, mica, and other ores.

The process is limited to granular material in the size range from 10 to 100 mesh. In this respect it differs from flotation, which functions best on material 48 mesh and finer. For best results the material should be well deslimed and should be conditioned with the agglomerating reagents at a high percentage of solids, 65 percent or greater. A collector is used that will selectively film the mineral to be agglomerated. In phosphate and limestone practice, this collector is usually a

TABLE 19-9 Generalized Operating Data for Superduty Diagonal-Deck Concentrating Table

Table No.	Feed	Feed size	Feed capacity, tons/hr	Speed, rpm	Stroke, in	Water with feed, gal/min	Dressing water, gal/min	Size of deck
6	Ore	¼ in.–35 mesh	2.0–10.0	275	1.25	30–150	10–100	6′5″ × 14′1″
6	Ore	35–150 mesh	1.0–2.5	285	0.75	16–40	5–20	6′5″ × 14′1″
6	Ore	Minus 150 mesh	0.25–1.0	300	.50	3–12	3–10	6′5″ × 14′1″
7	Coal	1½ in	15.0–25.0	270	1.25	125–210	55–90	8′¼″ × 16′9¼″
7	Coal	¾ in	10.0–15.0	280	1.00	60–85	20–35	8′¼″ × 16′9¼″
7	Coal	½ in	7.5–12.0	285	1.00	42–65	18–31	8′¼″ × 16′9¼″
7	Coal	⅛ in	5.0–7.5	290	0.75	28–42	12–18	8′¼″ × 16′9¼″
7	Coal	1⁄16 in	3.0–5.0	290	.75	15–28	9–12	8′¼″ × 16′9¼″

NOTE: To convert inches to meters, multiply by 0.0254; to convert tons per hour to kilograms per second, multiply by 0.252; to convert revolutions per minute to hertz, multiply by 0.0167; to convert gallons per minute to cubic meters per second, multiply 6.309×10^{-5}; and to convert feet to meters, multiply by 0.3048.

cheap fatty acid such as tall oil. In potash separation long-chain amines are used to film sylvite (KCl).

A bulk oil is always used in addition to the collector to give body to the film and to assist in forming agglomerates. In Florida practice, it is customary to use 0.14 to 0.23-kg/ton (0.3- to 0.5-lb/ton) tall oil and 1.8 to 23 kg/ton (4 to 5 lb/ton) of a 22°Bé fuel oil. Operating data for the agglomerate tabling of phosphate and potash ore are shown in Table 19-10.

Agglomerate tabling works best on simple ores consisting of two free minerals. It has several advantages over the usual tabling method in that it can be used to separate two minerals the difference in specific gravity of which is so small that an effective separation cannot be made by gravity separation alone. Tables treating an agglomerated feed have a considerably larger capacity than tables using untreated feeds, since the capacity of a table treating an agglomerated feed is limited only by the carrying capacity of the riffles. Disadvantages of the method that must be considered are the cost of the reagents used and the fact that if the mineral fraction filmed is the one to be sold, the oily film may be objectionable and must be removed.

SPIRAL CONCENTRATION

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Principle of Operation Spiral concentration of ores and industrial materials is based primarily on the specific-gravity differentials of the materials to be separated. The shape factor of the feed material is also important, and utilization of reagentized feed can change the apparent specific gravity of component minerals by forced attachment of air bubbles to mineral flocs. The best known spiral-type concentrator is the Humphreys spiral concentrator, which first proved its commercial feasibility in 1943. In that year an Oregon plant successfully demonstrated ability to recover chromium minerals from low-grade beach sand deposits.

The Humphreys spiral concentrator is a spirally shaped channel or launder with a modified semicircular cross section, as illustrated in Fig. 19-30. The standard spiral consists of five complete turns, but three-turn units are used in some instances when an unusually rapid and clean separation takes place, as in second-stage or cleaner spirals. There is a drop of 0.34 m (13.5 in)/turn as the flowing pulp progresses from the top to the bottom of the spiral. One spiral concentrator occupies about 0.37 m^2 (4 ft^2) of floor space and about 2.1 m (7 ft) of headroom measured from feed to discharge box. The optimum particle-size range of feed particles for spirals is about 10 to 200 mesh (2 to 0.074 mm).

As the feed slurry flows down the spiral channel, the particles with the highest specific gravity sink to the bottom and move inward toward the inside of the channel. The lighter-weight particles move to the outside and are carried away by the faster, more dilute pulp stream. At 120° intervals circular concentrate "ports," or openings, appear in the bottom of the channel near the inside edge, as illustrated in Fig. 19-31. There are 15 ports in a five-turn spiral, but usually more than half of them are blocked off with smooth stainless-steel disks in order to allow proper configuration of the concentrate stream and good washing of the concentrate. Wash water is available along the entire inside edge of the spiral, where it flows at the rate of 0.2 to 0.6 L/s (3 to 10 gal/min) in a separate wash-water channel. Thus the spiral provides repeated washing stages as the pulp flows down the channel. Generally the richest concentrate is withdrawn from the concentrate ports near the top end of the spiral. Concentrate ports are fitted with very simple stainless-steel "belt-disk splitters," which can split out the desired portion of the concentrate stream. As the gradually impoverished pulp flows down the spiral, wash water is proportioned from the wash-water channel by a series of notches and directed so as to wash repeatedly across the concentrate band and sweep out unwanted gangue particles. The lowest-specific-gravity solids wash outward, and the finest particles actually climb the sloping wall of pulp on the outside of the channel. The concentrate withdrawn from ports near the bottom end of the spiral is usually low-grade and, if liberated, may be recirculated to obtain additional recovery of values and a higher grade of concentrate.

Although the spiral concentrator is mechanically a very simple piece of equipment, the separating action taking place is complex. It involves centrifugal force, friction against the spiral surface, gravity, and the drag of the water.

TABLE 19-10 Operating Data for Agglomerate Tabling of Phosphate and Potash Ore

Type of table	Feed size	Feed capacity, tons/h	Table speed, r/min	Table stroke, in	Water with feed, gal/min	Dressing water, gal/min	Size of deck
No. 6 superduty diagonal deck	10–48 mesh	2.5–3.5	295	1.0	20–40	8–15	6′5″ × 14′1″

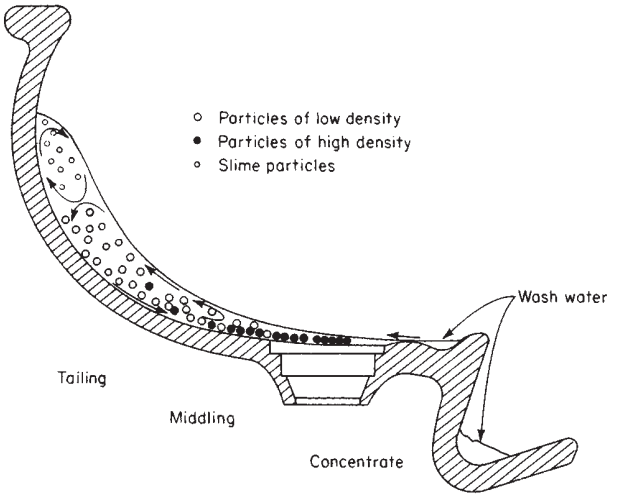


FIG. 19-30 Heavy-mineral separation in the Humphreys spiral concentrator.

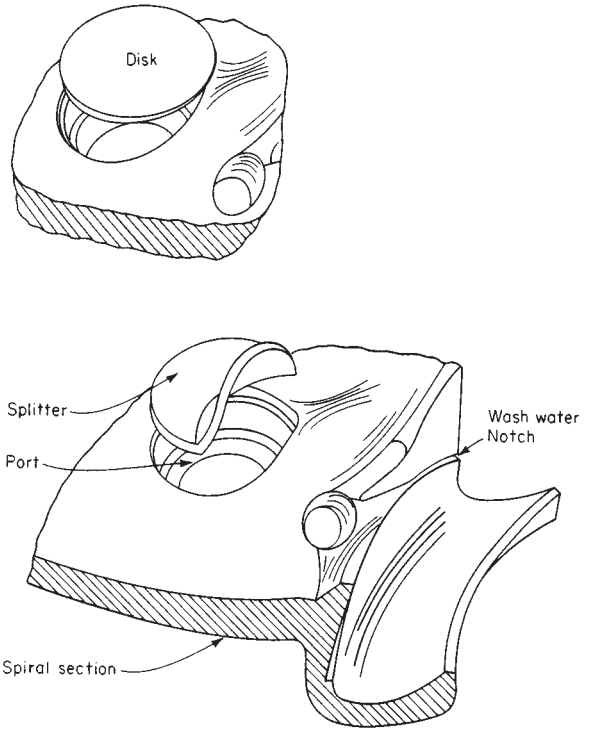


FIG. 19-31 Disks and splitters as used in the Humphreys spiral concentrator.

Basic Requirements for Spiral Concentration Minerals or materials of different specific gravity can usually be concentrated on spirals if the heavy particles do not exceed 10 mesh (2 mm) or are not finer than 200 mesh (0.074 mm). The size of the low-specific-gravity component is not critical when the values to be recovered are in the heavier-particle fraction. In this case the size of the light particles may range from 4 mesh (4.76 mm) to zero. The quantity of locked grain components (referred to as middlings in the mineral industry) that are present in a given pulp can be critical because this material is frequently recirculated and may eventually accumulate to a degree that will inhibit the separation operations. One solution to such a problem is continual removal of all or part of the middling stream to a grinding mill, followed by separate recovery of values in another spiral circuit or other concentrating machines.

Examples of good feed materials for spiral concentration are (1) beach sands that are processed for recovery of chromite, ilmenite, rutile, zircon, tin, and iron-ore minerals; (2) hard-rock iron ores in which good liberation of iron values occurs in the 10- to 200-mesh size range; (3) some mica and phosphate ores; (4) tailings from concentrating plants that contain heavy mineral components not recovered by flotation and other concentrating methods; and (5) some fractions of coal [minus 6-mm (¼-in) sizes] that can be upgraded by spiral concentration. The spiral used for coal cleaning has six complete turns with a more gradual slope [a 0.25-m (10-in) pitch]. The six turns require about the same headroom as the conventional five-turn spiral.

The spiral concentrator has shown unusual capability in the gravity processing of tailing streams from conventional magnetic and froth-flotation types of ore-processing plants. There are a number of minerals plants where some of the iron values are first recovered by spirals and the tailings are then sent to magnetic separators. There are also iron plants in which the reverse order of processing is used. In spirals the nonmagnetic iron minerals can be efficiently recovered as a high-grade product. An outstanding example of tailings processing in spirals is illustrated by a Colorado molybdenum-ore treatment plant. Spirals recover salable tungsten, pyrite, and tin concentrates from thousands of tons of flotation-plant waste every 24 h. There is no other known ore-processing method that can economically recover tin and tungsten values from this source. The crude ore contains only 0.03 percent tungstic oxide and a trace of tin. The tin occurs as the mineral cassiterite and the tungsten as the mineral hubnerite.

Operating Characteristics Spiral capacity can range from 0.12 to over 0.5 kg/s (0.5 to over 2 tons/h) of new feed. The grade of concentrate produced can be adversely affected by either too low or too high a feed rate. A good average feed rate for most spiral installations is 1.5 short tons of new feed per hour. The pulp density of spiral feed may range from 10 to 50 percent solids. If the values are contained in coarse heavy minerals, a high pulp density is preferred, whereas if the values are in fine-sized heavy minerals, it is better to use low pulp densities. Generally 20 to 30 percent solids by weight will constitute a suitable pulp feed.

Water Requirement The water requirement per spiral can range from 1.0 to 2.5 L/s (15 to 40 gal/min); this includes 0.2 to 0.6 L/s (3 to 10 gal/min) of water used in the wash-water channel. An attractive feature of the spiral is that reclaimed water can generally be used in all except the very final upgrading step.

Maintenance The only moving parts in spiral concentrators are those in the pumps that supply the feed and recirculate intermediate products. However, there are sometimes minor maintenance problems associated with the spiral trough itself. Some ores contain sharp particles of very abrasive minerals. The presence of these minerals in some ore causes rapid formation of deep grooves in the surface of cast-iron spirals. Wear grooves can be patched with a variety of plastic and metallic cements. Most spirals presently in service are made of cast iron with molded and vulcanized liners. These liners have successfully solved most wear problems.

Other than the wear problems, actual in-plant maintenance usually involves removal of wood, pieces of blasting wire, and other trash from the ports. When a reagentized feed is used, layers of oily reagents can build up on the spiral surface and sometimes require scrubbing for removal. With feeds containing oily reagents that attack rubber, abrasion-resistant alloy spiral sections are used.

Spirals have been manufactured from concrete, plastics, solid rubber, iron, and special iron alloys.

Operating Costs The operating cost of a spiral concentrator plant will be among the lowest costs of any ore-processing plant handling similar feed material. The only moving equipment parts involved are the pumps included in the flow sheet for the purpose of elevating feed and water to the spirals. One large pump can feed 100 or more spirals in a large plant. At a Canadian iron-ore plant twelve 0.14 m^3/s (2200-gal/min) pumps provide feed for 1152 rougher (or

first-stage) spirals. In many plants the second- and third-stage spirals are gravity-fed. Thus maintenance is largely limited to pump repair. When unusually abrasive ores are processed, maintenance of worn sections of the spirals can be extensive unless rubber coating or other abrasion-resistant materials are used on the wearing surfaces.

Labor requirements for a spiral plant are low and are governed primarily by the type of material being fed to the spirals. For example, a phosphate ore containing roots, leaves, and other trash will contain sufficient fibrous material to block concentrate ports, and generally prevent good spiral operation. When such an ore is processed, considerably more labor is required for cleaning and adjustments. Generally metallic ores are quite free of fibrous material that will hang up in the spirals, and one person can operate 100 or more spirals.

Power requirements for spiral plants are low, consisting primarily of pumping energy and possibly a thickener or other pulp-handling equipment associated with the flow sheet.

A typical summary of an approximate range of spiral concentration plant direct costs is given in Table 19-11.

DENSE-MEDIA SEPARATION

General References: Aplan and Spedden, "Viscosity Control in Heavy Media Suspension," *Proc. 7th Int. Miner. Process. Congr.,* New York, Sept. 20, 1964, Gordon and Breach, New York, 1965, p. 103. Browning, *Heavy Liquids and Procedures for Laboratory Separation of Minerals,* U.S. Bur. Mines Inf. Circ. 8007. Burton, "The economic impact of modern dense medium systems," *Minerals Engineering,* **4,** 225 (1991). Deurbrouck and Hudy, *Performance Characteristics of Coal-Washing Equipment: Dense-Medium Cyclones,* U.S. Bur. Mines Rep. Invest. 7673. Doyle, "The Sink-Float Process in Lead-Zinc Concentration," *AIME Symp. Lead Zinc,* St. Louis, 1970. "Mineral Engineering Techniques," *Chem. Eng. Prog. Symp. Ser.,* **50**(13), (1954). Mular and Bhappu (eds.), *Mineral Processing Plant Design,* 2d ed., Society of Mining Engineers, AIME, New York, 1980. Rodis and Cremer, "Why an Atomized Ferrosilicon?" *Min. World,* **22**(3), 36 (March 1960). Ruff, "New developments in dynamic dense-medium systems," *Mine & Quarry,* **13,** 24 (1984). Tippin and Browning, *Heavy Liquid Cyclone Concentration of Minerals,* U.S. Bur. Mines Rep. Invest. 6969 and 7134. Volin and Valentyik, "Control of Heavy Media Plants," *Pit Quarry,* **62,** 111 (December 1969). Walker and Allen, "Beneficiation of Industrial Minerals by Heavy Media Separation," *Trans. Am. Inst. Min. Metall. Pet. Eng., Min. Branch,* **184,** 17 (1949). Williams and Kelsall, "Degradation of ferrosilicon media in dense medium separation circuits," *Minerals Engineering,* **5,** 1 (1992).

Dense-media separation, also known as heavy-media or sink-float processing, is an adaptation of the common laboratory procedure for separating solids of differing specific gravities by immersing them in a heavy liquid of specific gravity intermediary between those of the solids, thereby causing the lighter particles to float while the heavier sink. However, in dense-media separation, the parting liquid is produced by dispersing relatively fine-grained solids of a high specific gravity in water and maintaining this pulp in suspension by light agitation. The method is very effective and can be used to separate solids with differences in specific gravity of as little as 0.005. It is often the only process needed for the removal of deleterious wastes from coal. The method is used extensively for beneficiating ore minerals, and it is finding increasing use for the processing of shredded automobile scrap and for the recovery of values from solid municipal waste.

Dense-media separation may be used to produce either a finished concentrate or an upgraded feed for subsequent processing. In the latter case, it provides a low-cost means to reject a significant amount of essentially barren waste at a coarse size.

Sink-float plants are usually custom-designed for each individual application. However, for coal beneficiation modular units are available. For most large mineral-processing applications the plants will be permanently located for easy access of feed and disposal of waste, but for smaller coal and aggregate operations the plants are often constructed with the anticipation of relocation when the deposits have been depleted.

TABLE 19-11 Approximate Range of Direct Costs for Spiral Concentration

Cost element	Cents per short ton of spiral feed
Labor	3.0–5.0
Power	1.6–3.0
Maintenance	2.0–3.0
Depreciation	2.8–4.0
Total	9.4–15.0

The response of any given feed to sink-float processing can be accurately established in the laboratory by testing with various heavy liquids. The liquids generally used for this purpose are listed in Table 19-12. These halogenated hydrocarbons are mutually miscible, which enables the preparation of almost any pulp density attainable in a commercial plant. Heavy-liquid test work provides the basis for specifying the optimum screen size for the preparation of the feed.

Continuous pilot-plant test runs are generally recommended to verify the laboratory results and to establish criteria for plant design. Facilities for these runs are available at a number of minerals-processing research centers.

Feed Preparation and Feed Size The ability to achieve a separation of different solid particles on the basis of density, as in all physical separation, depends on the degree to which the particles are liberated (detached) from each other. Liberation can be achieved by breaking the material in a manner that causes it to fracture and free the individual grains of the constituents to be recovered. The degree of separation that can be realized by the dense-media process will depend on the degree of liberation of the individual grains.

There will be an optimum size reduction of the feed material for the dense-media process. This size range can depend on the overall objectives of its use. For example, if the process is to be used in conjunction with a subsequent separation method such as flotation, the intent may be more the rejection of barren waste material at a relatively coarse size and at high recovery of the values, although the resulting grade from the dense-media operation may still be low. On the other hand, if the concentrate grade must be high, a finer degree of liberation will be needed at some loss in recovery. The initial test work can establish the so-called grade versus recovery limitations of the dense-media operation for the specific material of interest. This testing should recognize that the dense-media process is not effective for treating material which contains any substantial amount of particles smaller in size than about 0.5 mm (20 to 28 Tyler mesh).

The largest size that can be treated depends mostly on the dimensions of the separating vessel; coal up to 0.3 m (12 in) has been successfully processed in a drum separator of the type illustrated in Fig. 19-32. Complete removal of fines is usually necessary to ensure proper viscosity of the media. Fines increase viscosity and slow the separation process.

The feed-preparation screen between crusher and separatory vessel may be of either the revolving or the vibrating type. Wash water is applied only to the feed end of the screen so that the process feed will enter the separator moist but without any free water, which would lower pulp density. In a few instances it has been found advantageous to provide for surge storage between screen and separator to drain off further excess water.

A typical flow sheet is shown on Fig. 19-33.

Preparation of the Media Various solid materials have been used to prepare the media. In the initial development of the process, a suspension of sand and also mixtures of barite and clay were used for separating coal from slate. Galena (lead sulfide mineral) was also used

TABLE 19-12 Liquids Used to Test Feeds

Name	Specific gravity, 25°C
Methylene iodide	3.33
Tetrabromoethane	2.96
Bromoform	2.89
Tribromoethane	2.61
Methylene bromide	2.48
Ethylene dibromide	2.17
Methylene chlorobromide	1.92
Pentachloroethane	1.67
Carbon tetrachloride	1.59
Trichloroethylene	1.46
Ethylene dichloride	1.26

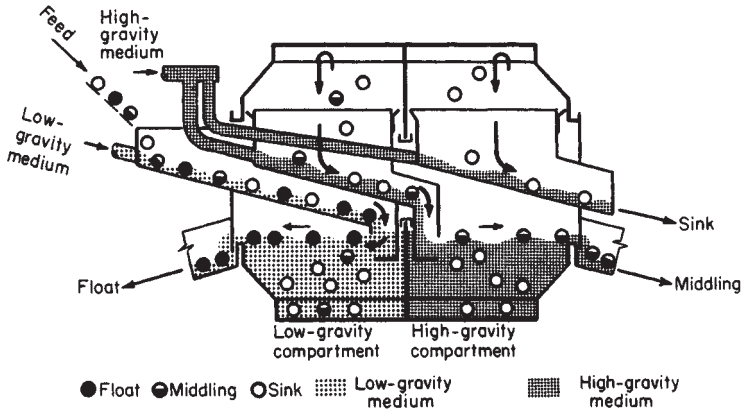


FIG. 19-32 Revolving-drum-type dense-media separatory vessel. (*Courtesy of Western Machinery Co.*)

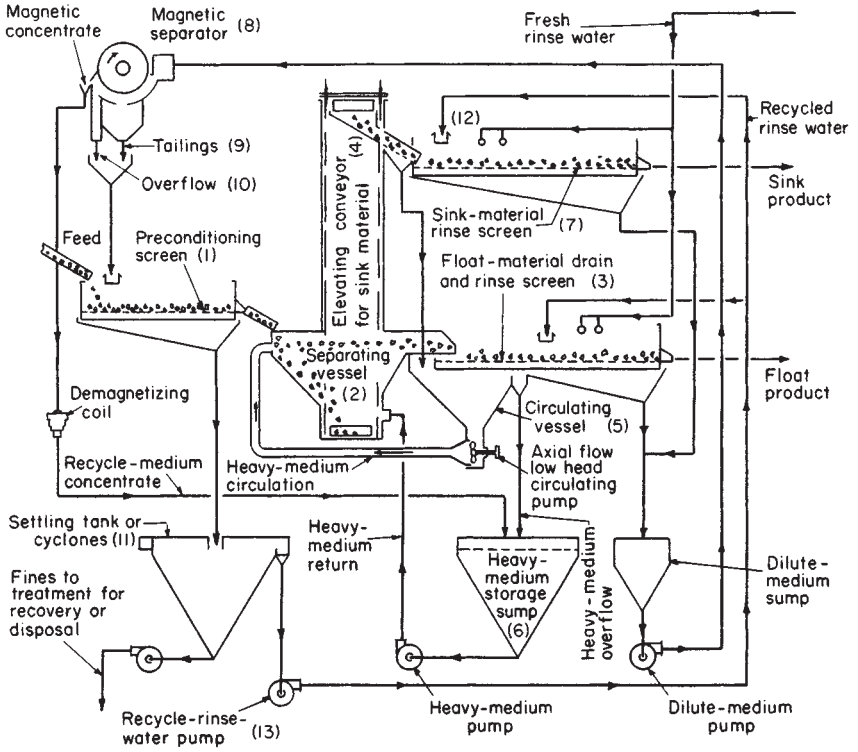


FIG. 19-33 Typical dense-media flow sheet for a coal-cleaning plant. (*Courtesy of Process Machinery Division, Arthur G. McKee Co.*)

to achieve a higher pulp density. In present processing, iron-based particles such as magnetite and ferrosilicon are preferred because they offer suitable density, high resistance to attrition, and ease of recovery by magnetic methods. With magnetite, a pulp density 2.5 times that of water can be obtained. Ferrosilicon can provide a density factor of 3.3, which is effective for separating most gangue constituents from metallic ores. Both materials might be used to obtain intermediate media densities.

Media-Particle Size The size of the media particle is important. A relatively coarse medium (minus 100 mesh) is commonly used in larger-volume static-type separators such as cones. However, in dynamic separators, a much finer size is desirable. Ground magnetite or atomized ferrosilicon is advantageous in this application. The latter is produced by pouring molten ferrosilicon into an atomizing chamber, where a jet of steam forms the alloy into spherical particles. These particles are more resistant to wear than are the particles in a ground product and cause less abrasion to the equipment. Atomized ferrosilicon permits pulp densities above about 3.4-density factor.

Custom-ground natural magnetite is available in many size ranges. Table 19-13 gives a typical specification sheet. Cost is based on truckload quantities in 45.4-kg (100-lb) paper bags, FOB Frazer, Pennsylvania.

TABLE 19-13 Typical Size Distribution of Ground Natural Magnetite*

Product grade	Percent retained by weight for mesh size				1978 cost
	100	200	325	Less than 325	
A	0.6	12.0	17.8	69.6	$72
B	0.1	1.0	7.6	91.4	$74
C	5.0	22.0	23.0	50.0	$72
D	6.0	29.5	22.9	36.3	$71
E	0.1	0.4	1.9	97.7	$85
G	0.2	6.2	15.5	78.1	$74

*Foote Mineral Company.

Pulverized ferrosilicon containing approximately 15 percent silicon is available from the Foote Mineral Company and from Carborundum Co. in the sizes and at the prices shown in Table 19-14. Cost is based on truckload quantities in 227-kg (500-lb) steel drums, FOB Keokuk, Iowa, and Niagara Falls, Ontario.

Atomized ferrosilicon is at present available only from West Germany through American Hoechst Corp. in the sizes shown on Table 19-15. Costs vary with the exchange of U.S. dollars to deutsche marks but will be around $770 per metric ton, FOB Germany (1978 estimate).

Chemical Additives The use of chemical additives in sink-float processing is not common except for the use of lime to prevent oxidation and decomposition of the medium. A small amount of clay is sometimes added to improve the kinetic stability of the suspension.

Considerable laboratory work has indicated that the use of a dispersant such as sodium hexametaphosphate may assist in the stabilization of the medium; more recent data report the beneficial effect of the addition of polymers that reduce media viscosity while simultaneously producing a very low settling rate of the ferrous compound. This should be of great value for difficult separations, but at present no data are available from commercial operations.

Separating Vessels Many different types of separating vessels have been proposed and used for sink-float separation. For applications at coarse sizes involving a high ratio of float to sink or a high gravity differential, as in the case of coal, trough-shaped vessels (as shown in Fig. 19-34) or rotating-wheel separators are commonly used. However, for the beneficiation of most ores, other types of separators have found general acceptance. The optimum design for any given ore will depend on such variables as the rate of feed, the size of feed particles, the ratio of float to sink, and the gravity differential between the solids to be separated. Separators are classified as either static or dynamic, depending on whether or not centrifugal force is applied.

TABLE 19-14 Typical Size Distribution of Pulverized Ferrosilicon

Particle size; mesh size less than	1978 cost range
48	$245–279
65	$248–282
100	$252–291
200	$289–400

Drum Separators Very coarse solids, up to 0.3 m (12 in), are often processed in a drum separator of the type shown in Fig. 19-32. This is similar to a ball-mill shell with lifters permanently attached to the wall. Medium and feed enter at one end, and the float product flows out through the discharge trunnion, while the sink is lifted by the rotation of the drum to a stationary launder, through which it is flushed out. Modifications of this type include division of the shell into two compartments, which permits simultaneous operation at two different pulp densities resulting in various grades of products. The two-compartment revolving drum is illustrated in Fig. 19-32.

Drum separators have capacities up to 250 kg/s (900 t/h), cone separators to about 125 kg/s (500 t/h), and dynamic separators a maximum of 28 kg/s (100 t/h); however, these can readily be manifolded for any required tonnage. Economics will dictate the minimum tonnage for which a plant would be justified; several plants of 2.8-kg/s (10-t/h) capacity have been built.

Cone Separators Feed materials in the intermediate sizes, 0.1 to 0.01 m (4 to 0.5 in), may be processed in cone separators as shown in Fig. 19-35. These have a large surface area and increased volume pulp, which permit longer retention time than that of most other types of separators; this is a great advantage when separating solids of small gravity differential. The feed is introduced into the cone at a point below the pool surface and as far from the overflow baffle as possible. Slow-moving scrapers prevent a buildup of medium on the cone wall, provide the necessary agitation to prevent settling of the medium, and push the float particles toward the overflow weir. The sink product is removed from the cone bottom by rock pump, internal air lift, or external air lift. Mechanical elevators of the screw or bucket type have also been used but require more maintenance.

Cyclone Separators Finer feed solids, from 0.04 to 0.0005 m (1.5 in to 28 mesh), may be treated in dynamic separators of the Dutch State Mines cyclone type (Fig. 19-36). In cyclone separators, the medium and the feed enter the separator together tangentially at the feed inlet (1); the short cylindrical section (2) carries the central vortex finder (3), which prevents short circuiting within the cyclone. Separation is made in the cone-shaped part of the cyclone (4) by the action of centrifugal and centripetal forces. The heavier portion of the feed leaves the cyclone at the apex opening (5), and the lighter portion leaves at the overflow top orifice (6).

The sharpness of separation of the mineral from the gangue is dependent on (1) the stability of the suspension, which is influenced by the size of the medium; (2) the specific gravity of the medium; (3) the cleanliness of the medium; (4) the cone angle; (5) the size and ratios of the internal openings in the cyclone (inlet, apex, and vortex); and (6) the pressure at which the pulp is introduced into the cyclone. A 20° cone angle is the most common. Cyclone diameter will be determined by the separation to be made as well as by the capacity required. The 0.5- and 0.6-m (20- and 24-in) cyclones are most common in coal plants, whereas multiple cones of 0.25- or 0.3-m (10- or 12-in) diameter are used in higher-gravity separations.

Dense-media cyclones are generally operated in the $(0.7–1.0) \times 10^6$·Pa (10–15-lbf/in^2) range. It is not advisable to go below $(0.4–0.56) \times 10^6$ Pa because the recovery of low-specific-gravity material and the rejection of impurity are improved at higher pressures,

TABLE 19-15 Size Distribution of Atomized Ferrosilicons

Particle size, greater than Tyler mesh	Manufacturers' grade distribution					
	Extra coarse	Coarse	Fine	Cyclone 60	Cyclone 40	Cyclone 20
48	15–0	5–0				
65	25–7	8–2	4–0			
100	42–20	22–7	8–2	3–0		
150	55–35	35–17	22–5	8–0	3–0	
200	70–50	50–35	30–15	20–5	8–3	2–0
Particle size, less than Tyler mesh						
200	30–50	50–65	70–85	80–95	92–97	98–100
325				40–60	70–85	90–100
625				10–20	40–55	70–80

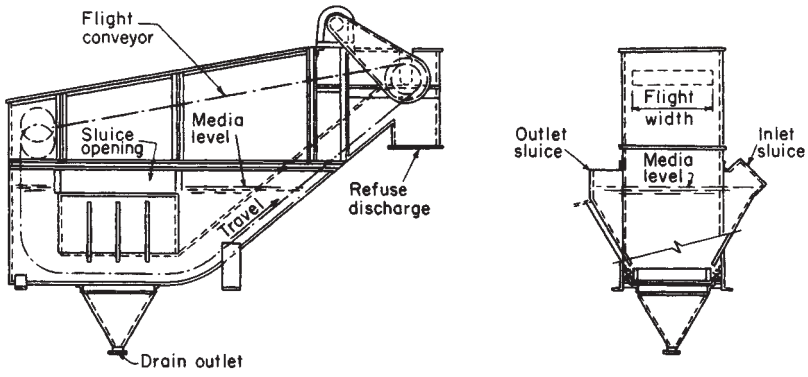


FIG. 19-34 Drag-tank-type dense-media separatory vessel. (*Courtesy of Link-Belt Co.*)

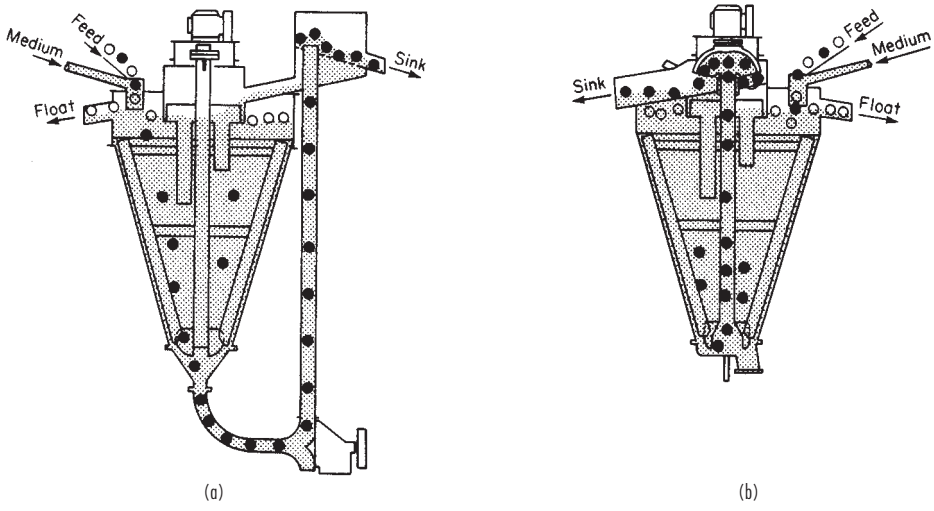


FIG. 19-35 Dense-media cone-vessel arrangements. (*a*) Single-gravity two-product system with pump sink removal. (*b*) Single-gravity two-product system with compressed-air sink removal. (*Courtesy of Process Machinery Division, Arthur G. McKee Co.*)

especially for the finer sizes. Pressures as high as 2.5×10^6 Pa (36 lbf/in^2) have been used, and they increase capacity but accelerate wear. Residence time of the ore particles is very short in the cyclone, and a large volume of medium is circulated for each ton of feed treated in the cone. Loss of media is higher in cyclone plants because of the finer media required and the additional volume encountered in these plants. Media loss may be 2 to 5 kg/ton (5 to 10 lb/ton) of ore treated in cyclone plants, as compared with 0.2 to 0.8 kg/ton (0.5 to 1.5 lb/ton) in coarse, static heavy-medium circuits. Cyclone-plant labor requirements are low and efficiency is high. A 0.6-m (24-in) heavy-medium cyclone can handle 75 tons of coal per hour.

Dyna Whirlpool A unique vessel design for capacities up to 100 t/h has been developed by the American Zinc Co. The separation occurs in a cylindrical-shaped separatory vessel maintained in an inclined position from horizontal. This system, known as the Dyna Whirlpool (DWP) process, provides for separate entry of the medium and the feed solids, as illustrated in Fig. 19-37. A distinct feature of this separator is that the feed enters the separator via gravity flow. Feed size may range from 0.05 to 0.0002 m (2 in to 65 mesh). Magnetite or ferrosilicon is generally used.

Process Control As is the case in all concentration processes, optimum results will be obtained under steady operating conditions. Because of the simplicity of the dense-media process, these can readily be maintained.

Uniformity of the rate of feed will be ensured by a constant-weight feeder; density control may be automatically obtained through a measuring probe on the media-return line that adjusts delivery of the necessary volume of media from the densifier or media thickener; the viscosity can be controlled automatically by continuously testing a predetermined volume of return media and adjusting the divider under the drainage screen for media cleaning as needed; pH control can be automated by conventional methods.

Notwithstanding the possibility of such automation, many successful operations depend almost entirely on manual sampling. Density determinations of the pulp on the media-return line and on each of the drainage screens are made at scheduled intervals, and the operator adjusts the media flow as needed.

Costs Because sink-float processing is applied to relatively coarse particles and is a single-pass operation, capital and operating costs are usually considerably lower than would be required for a flotation or a gravity mill of the same capacity. A large flow of water is required for feed preparation and for media recovery, but almost total recovery for recirculation is possible. A minimum of two job-trained operators per shift is generally required by law, but these would be able to attend several separators at almost any feed rate.

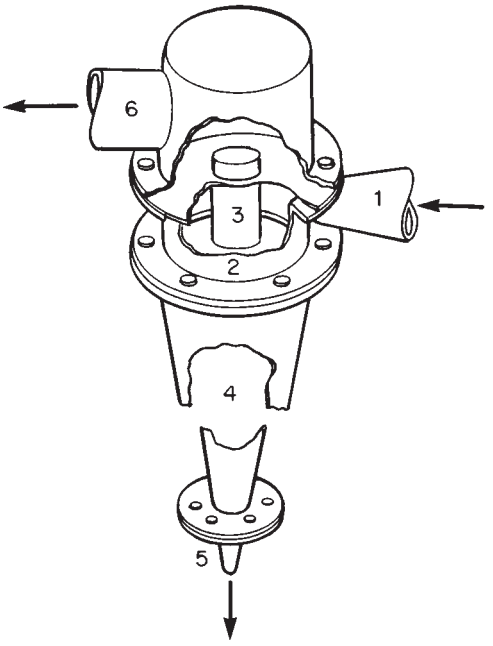


FIG. 19-36 Dutch State Mines cyclone separator.

Estimates for a 30-kg/s (100-ton/h) plant using a dynamic separator is approximately $350,000 (1978), exclusive of power, water, compressed air, crushing, foundations, and housing; installed power for such a plant will be about 298 kW (400 hp).

Direct operating costs usually vary between 30 cents and $1 per ton of feed, depending on hourly tonnage and on media recovery. Media losses are usually higher in a dynamic than in a static separator, mainly because a finer particle size is required. Media loss may be from 2 to 20 kg/t (5 to 10 lb/ton) of mixture processed in a cyclone plant compared with a static plant, which generally operates with media losses of an order of magnitude lower.

MAGNETIC SEPARATION

General References: Kolm, Oberteuffer, and Kelland, "High-Gradient Magnetic Separation," *Sci. Am.*, **233**(5), 46–54 (November 1975). Lawyer and Hopstock, "Wet Magnetic Separation of Weakly Magnetic Materials," *Min. Sci. Eng.*, **6**(3), 154–172 (July 1974). Marston, "The Use of Electromagnetic Fields for the Separation of Minerals," World Electrical Congress, Moscow, 1977. Taggart, *Handbook of Mineral Dressing*, 2d ed., Wiley, New York, 1945.

The principles of magnetic separation have been applied commercially for nearly 100 years. Applications range from the removal of coarse tramp iron to more sophisticated separations, such as the elimination of weakly magnetic iron-stained particulates from paper-coating clays. The application of magnetic-separation methods to weakly magnetic particles has been made possible by recent advances in separator design. Magnetic separators now have a great many industrial applications and range in size from small laboratory-scale devices to those capable of processing hundreds of tons hourly.

Selecting the best separator for a specific application requires an understanding of basic principles of magnetism plus an evaluation of separator capability on the basis of design and application variables such as type of material to be processed, wet or dry processing, particle-size range, magnetic characteristics of the feed, desired throughput rate, etc.

Principles of Magnetic Separation Any particle introduced into a magnetic field will become magnetized to some extent and act as a magnetic dipole. Depending on the magnetic characteristics of the material, it can be classified as ferromagnetic, paramagnetic (magnetically attracted), or diamagnetic (repelled by a magnetic field). Ferromagnetic substances (e.g., iron, nickel, and cobalt) may be permanently magnetized and have strong magnetic moments per unit volume. Paramagnetic substances are further classified as strongly or weakly magnetic according to the strength of the magnetic moment produced per unit volume in the external magnetic field.

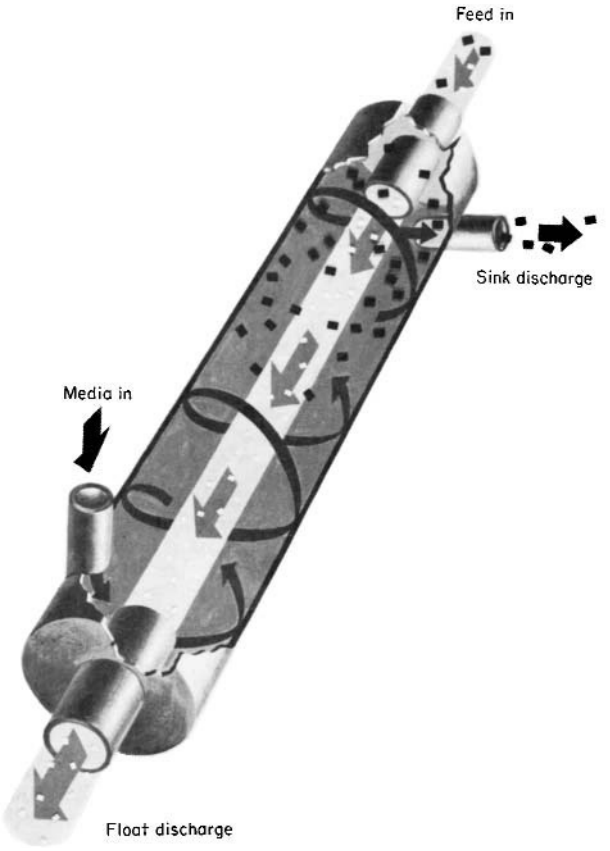


FIG. 19-37 Dyna Whirlpool separator. (*Courtesy of American Zinc Co.*)

A magnetic field and magnetic-field gradients are produced in a variety of ways and vary in both field geometry and strength. The magnetic field of a magnet is the space through which its influence extends. It is mapped by the lines of magnetic force. A magnetic field is considered uniform or homogeneous when these lines are parallel and equally spaced. It can be noted in Fig. 19-38*a* and *b* that neither the bar (permanent) magnet nor the coils plus iron magnet typical of the C-frame magnet type can produce a uniform magnetic field.

The intensity of the magnetic field H is measured in amperes per meter. For a single-layer solenoid, at any point along its axis the magnetic field intensity is

$$H = \tfrac{1}{2}NI(\cos\theta_2 - \cos\theta_1) \qquad (19\text{-}8)$$

where H is measured in amperes per meter, A/m; N is the number of turns per unit length or the number of turns per meter; I is the current per turn in amperes, A; θ_1 and θ_2 are the angles included between the axis and the lines drawn from the measured point to its near and far edges.

The magnetic flux density is

$$B = \mu_0(H + M) \qquad (19\text{-}9)$$

Flux density is calculated as the permeability of free space times the sum of the magnetic-field intensity and the induced magnetization

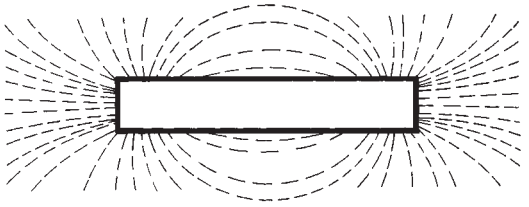


FIG. 19-38*a* Lines of force surrounding a bar-type magnet.

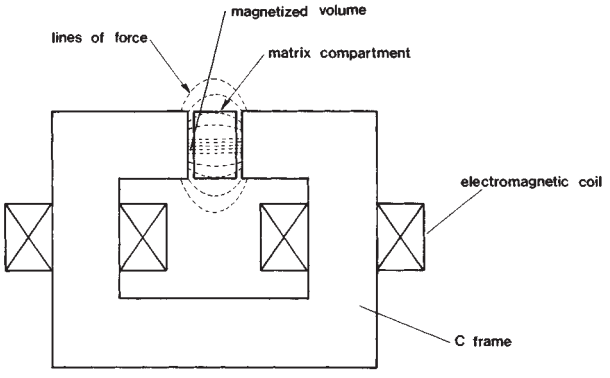


FIG. 19-38*b* Lines of force produced by a C-frame magnet (coils and iron-magnet surface).

observed whenever a magnetic material is placed in a magnetic field; it is measured in teslas, T.

The strength of the induced magnetization is equivalent to M dipoles per cubic meter where μ_0 is the permeability of free space, equal to $4\pi \times 10^{-7}$, N/A^2; and M is the magnetization, A/m.

Another method for calculating B is

$$B = \mu H \tag{19-10}$$

where μ is the permeability of the material.

The magnetic susceptibility of a material (χ, volume susceptibility) is dimensionless and is defined as the ratio of induced magnetization to magnetic field intensity. It is expressed as

$$\chi = M/H \tag{19-11}$$

Thus,

$$B = \mu_0 H(1 + \chi) \tag{19-12}$$

Specific magnetic susceptibility (ψ) is

$$\psi = \chi/\rho \tag{19-13}$$

where ρ is material density.

Paramagnetic substances have positive susceptibilities, and induced magnetization augments the magnetic-flux density within the substance. Diamagnetic materials have negative susceptibilities, and an induced field in this case cancels part of the magnetic-field intensity.

Permeability (μ), which is often used, albeit imprecisely, in referring to ferromagnetic substances, is the ratio of the magnetic-flux density to the magnetic-field density.

$$\mu = B/H \tag{19-14}$$

Relative permeability is μ/μ_0.

In cgs units,

$$B = H + 4\pi I \tag{19-15}$$

$$K = I/H \tag{19-16}$$

$$K = \chi/4\pi \tag{19-17}$$

Table 19-16 shows the magnetic susceptibility of minerals and elements. Magnetization of various materials is directly dependent on

TABLE 19-16 Magnetic Susceptibility of Elements and Minerals

Substance	Susceptibility, 10^{-6} cgs	Substance	Susceptibility, 10^{-6} cgs
Aluminum	+10.5	Ferberite	+39.3
Al_2O_3	−37.0	Galena	−0.4
Apatite	+1.0 to +18.0	Garnierite	+30.7
Aragonite	−0.4	Gold	−28.0
Asbolan	+150.0	Ilmenite	+15.45 to 70.0
Azurite	+12.2 to +19.0	Lead	−23
Anatase	+0.96 to +5.60	Malachite	+10.5 to +14.5
Beryl	+0.4	Millerite	+0.21 to +3.85
Braunite	+35.0 to +150.0	Molybdenite	+4.93 to +7.07
Biotite	+40.0	Molybdenum	+89.0
Barite	+10.0	Platinum	+201.9
Barite (pure)	−71.3	Rutile	+0.85 to +4.78
Brannerite	+3.5	Scheelite	+0.13 to +0.27
Chromium	+180.0	Siderite	+65.19 to +103.81
Chromite	+125.6 to +450.0	Titanium	+150.0
Cobalt	Ferromagnetic	Tungsten	+59.0
Cobaltine	+2.0	Uranium	+395.0
Cobaltite	+0.34 to +0.64	Vanadium	+255.0
Columbite	+32.55 to +37.20	Vanadinite	−0.2 to +0.27
Copper	−0.1	Wolframite	+42.2
Chalcopyrite	+1.0 to +5.0		

NOTE: Extensive listing of magnetic susceptibilities of elements and organic and inorganic compounds can be found in G. Foex, *Tables de constantes et donnes numériques,* Massou et Cie., Paris, 1957.

two factors: (1) the degree of magnetic susceptibility and (2) the applied magnetic-field intensity. It can be seen in Fig. 19-39 that ferromagnetic materials quickly become magnetically saturated and that an increase in magnetic-field intensity will have no effect after a certain point. For paramagnetic materials (e.g., hematite), which are more difficult to magnetize, the magnetic-flux density is directly proportional to the magnetic-field intensity, and some of these substances, practically speaking, cannot be saturated.

In addition, the magnetic characteristics of a material can change as a function of stress (e.g., unannealed series 316 stainless steel can be magnetic after machining), temperature, pressure, and physical and chemical treatment. Therefore, when two paramagnetic materials with similar magnetic susceptibilities are to be separated, the possibility that pretreatment will facilitate subsequent separation should be studied.

A magnetic field exerts a force on each of the two poles of a dipole (particle), forcing it to align itself with the lines of magnetic force.

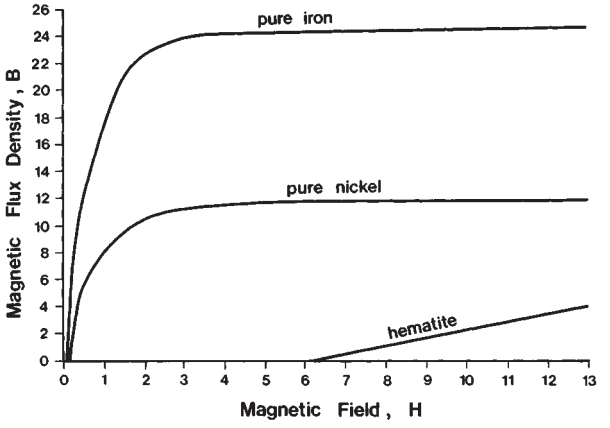


FIG. 19-39 Magnetization curves for ferromagnetic and paramagnetic materials.

These are exerted in opposite directions, and if the magnetic field is uniform, they will be equal. Therefore, the net force on the dipole will be zero. However, if the field varies in space (has a gradient), the force on the dipole will be greater in the direction of the higher field and will be proportional to the magnetic-dipole moment and the magnitude of the magnetic-field gradient.

A model of the forces operating in such a case is shown in Fig. 19-40, where

$$F_m = m\, dB/dz \tag{19-18}$$

$$F_d = 3\pi\eta b v \tag{19-19}$$

where F_m = magnetic tractive force
F_d = hydrodynamic drag force
F_g = gravitational force
m = magnetization characterization of the particle ($m = \chi HV$)
H = magnetic-field intensity
dB/dz = magnetic-field gradient
η = fluid viscosity
b = particle diameter
v = fluid velocity
V = particle volume
χ = magnetic permeability of particle

In order to retain the magnetic fraction of the material in the collection volume of the separator it is necessary that

$$F_m \geq F_d + F_g \tag{19-20}$$

The preceding analysis shows that density is important and cannot be influenced and that particle size is of extreme importance, as the magnetic force F_m is directly dependent on the b^3 of the particle while the drag force F_d is dependent on b. This means that separations between particles with close magnetic susceptibilities can be successfully performed only if the particle-size distribution is within a relatively narrow range. The influence of gravitational force is dependent on the relative direction of the slurry flow. [Buoyant forces are neglected in the relationship expressed in Eq. (19-20).]

It should be noted that effective magnetic separation requires that particles of different species be liberated from each other. It is also important that the finest possible matrices (filamentary type) be used because these produce the highest magnetic-field gradients. The use of high-gradient-producing matrices can substantially reduce the magnetic-field intensity (magnet strength) required to gain the same separation results, thus lowering both capital investment and process costs. The most economical results are achieved when the diameters of the matrix filaments are matched to the size of the particulates being processed.

Factors which adversely influence the separation of very fine particle systems are brownian motion and London forces. However, it is possible to counter these forces by the use of dispersants, temperature control, and so on.

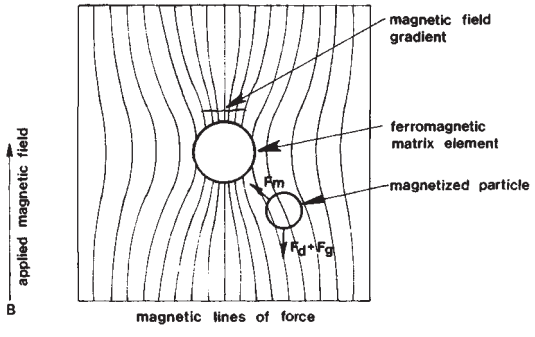


FIG. 19-40 Model of particle-capture forces.

Equipment Separator designs differ for the various types of materials to be separated. In general, magnetic separation devices can be grouped as follows:

Grate-Type Magnets This type of device consists of a series of tubes (often of stainless steel) which are packed with ceramic magnets and installed in a trap perpendicular to the fluid-flow direction. Grate magnets are used for the wet or dry removal of tramp coarse or fine iron. The various available equipment designs include self-cleaning grates, wing-and-drawer-type magnetic grates, permanent magnetic grates, vibratory grates, and rota-grates. Each of the designs is manufactured in a range of sizes, with single or multiple rows (banks) of magnetic tubes. Applications include ferrous traps for slurries such as detergents (e.g., in chemical plants), sugar and candy (e.g., in food plants), ink recycling (e.g., in printing operations), or pulp in paper mills.

Grates may be installed in all circuits of dry, pulverized material where contamination or accidents may occur from tramp or fine iron.

Plate Magnets and Magnetic Humps These devices are used to remove tramp iron from materials being conveyed pneumatically or falling in gravity flow. Tramp iron is removed by being trapped against a magnetized plate. This type of magnet must be cleaned periodically. A chute angle of 45° is recommended. The plate magnet should be close to the feed point to eliminate the influence of velocity. Complete lines of plate magnets and magnetic humps are offered by many manufacturers.

Plate magnets, which are used in chutes, can be either permanent magnets or electromagnets. For the permanent type, magnet width extends to 1.23 m; there is a maximum width of 2.85 m for electromagnets. Capacities are approximately 250 m^3/h for each meter of width, at a 45° angle, with the magnet located in the bottom of the chute approximately 0.6 m from the top and material introduced at a slow velocity. Capacity varies with the size of the tramp-iron particles to be removed and with the angle of the chute (see Table 19-17).

Lifting Magnets These devices operate in either a continuous or a cyclic manner. Continuous devices usually have a belt which moves over the lifting magnetic poles to carry the magnetized particles into a region of low or zero magnetic field, where they are released. Depending on the design of the poles, these units can be either high- or low-intensity devices. Figure 19-41 shows the in-line and cross-belt methods for installing a lifting magnet above a conveyor belt.

Cross-belt magnetic separators are based on the same principle as lifting magnets. Although these units have relatively low capacities, the same unit can produce selective separations with different products by using different pole gaps and field strengths. (See Fig. 19-42.)

The magnet designs shown in Figs. 19-41 and 19-42 are used for tramp-iron removal. Suspended magnets are positioned from 5 to 10 cm above the highest point of the material on the conveyor and may be designed to be self-cleaning. Sizes for devices of this type range up to 2.8/1.6 m. The installation shown in Fig. 19-41*a* is often preferred because it requires a less powerful magnet and can clean material from a higher-speed conveyor belt (over 1.75 m/s). For self-cleaning units, the belt is run at up to 2.5 m/s.

Drum and Pulley Magnets Since Thomas Edison invented and developed the magnetic pulley for the concentration of nickel ore, drums and pulleys have become the most common types of magnetic separators. These devices can be built with either a permanent magnet or an electromagnet, and the drum separator can operate with

TABLE 19-17 Tramp-Iron Removal with Plate Magnet, 0.6 m from Top*

Particle size	Relative capacity, percent		
	Chute angle, 35°	Chute angle, 45°	Chute angle, 60°
Over 30 g (1 oz)	125	100	75
Over 8 mesh (2.38 mm) to 30 g	100	75	45
Under 8 mesh (2.38 mm)	33	25	10

*Courtesy of Eriez Magnetics.

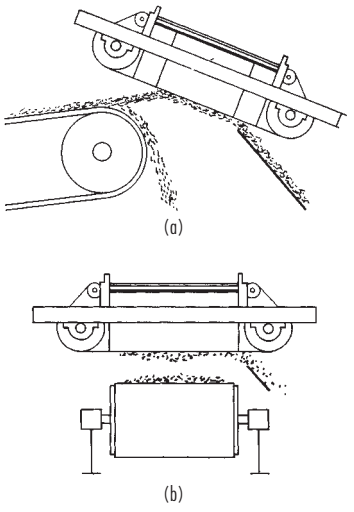


FIG. 19-41 Types of lifting magnets. (*a*) In-line lifting magnet. (*b*) Cross-belt lifting magnet. (*Courtesy of Eriez Magnetics.*)

either dry or wet feeds. Figure 19-43 is a schematic for mounting a magnetic pulley.

Dry magnetic drums can be designed to perform as lifting magnets or pulleys. Magnetic drum devices have stationary magnets; pulley drums rotate. Other schematics of possible arrangements are presented in Fig. 19-44.

In the drum-separator category, several specialized devices are worthy of mention.

Alternating-polarity drum separator. This device is used for the treatment of coarse material (minus 40 mm, plus 0.15 mm) containing strongly magnetic particles when a high-grade concentrate is required. The capacity of this device varies with feed-particle size, up to 100 t/(h·m).

Unigap drum separator. This device is used for materials finer than 6 mm at feed rates of up to 10 t/(h·m).

High-speed, low-intensity drum magnetic separator. This device is designed to handle very fine material (minus 0.15 mm and finer) to produce a high-grade magnetic concentrate.

Depending on the required results—high recovery of magnetics or high-grade concentrates (clean magnetics)—wet drum separators are designed to work in concurrent, countercurrent, or counterrotating fashion by using one or more drums in any possible combination. Figure 19-45 presents schematics of these wet drum magnetic separators.

Magnetic pulleys. These vary in size from 0.203 to 1.219 m in diameter and from 2.03 to 1.526 m in width. The acceptable depth of the material on the conveyor belt depends on the diameter of the pulley and the linear velocity of the belt (see Table 19-18). Table 19-19 indicates the maximum capacity for such units. Depending on the application, the correction factors given in Table 19-20 should be applied. For sizing and maximum efficiency, multiply the actual volume of material to be handled by the correction factor shown and select the magnetic pulley having a capacity equal to or greater than the resultant volume.

Wet Drum Magnetic Separators These devices are used for the concentration of strongly magnetic coarse particles. The size of the separator is influenced by several variables: slurry volume, percent solids in the slurry, percent magnetics in the slurry, required recovery of magnetic particles, and required concentration of magnetic product. This type of separator is built by several manufacturers; drum sizes range from 0.023 to 1.2 m in diameter, with widths up to 3.0 m. The concurrent type can process slurries with 20 percent solids by weight for single-drum separators and with 35 to 45 percent for units with two drums. Recommended maximum particle size is 6 mm (¼ in), but with special tanks these devices can handle even coarser material. Countercurrent-type separators can handle particles finer than 0.8 mm (20 mesh) and obtain optimum results with slurries containing about 30 percent solids. This design has the advantage of being able to handle wide fluctuations in throughput. The counterrotating separator is recommended for applications in which recovery is more important than grade. This unit can handle particles up to 3 or 4 mm (⅛ in) in size, but with less satisfactory results for particles finer than 0.5 mm and slurries containing 30 to 40 percent solids by weight. Figure 19-46 shows a gauss (tesla) chart for a 1.2-m-diameter wet drum separator. The influence of drum diameter in separation is shown in Table 19-21 and in Fig. 19-47. These data result from the processing of a partially martised magnetite ground to 75 percent minus 0.044 mm (325 mesh). The influence of drum diameter and grind in separator capability is summarized in Table 19-22. Figure 19-48 shows the influence of drum diameter on investment. The **installed cost** of a wet single-drum magnetic separator can vary between $25,000 and $75,000 per meter of magnet width, depending on the design, dimensions, and manufacturer. Multiple-drum costs increase in about direct proportion to the number of drums required. **Maintenance costs** per year vary between 3 and 5 percent of the initial investment.

Induced-Roll Separators These devices, which have been in commercial use since 1890, handle only dry, granulated material. They are similar to drum separators, with the difference that the cylinder rotates in the gap of an electromagnet. Magnetic-field gradients are obtained by creating sharply edged ridges on the surface of the cylinder or by constructing a cylinder of alternate magnetic and non-

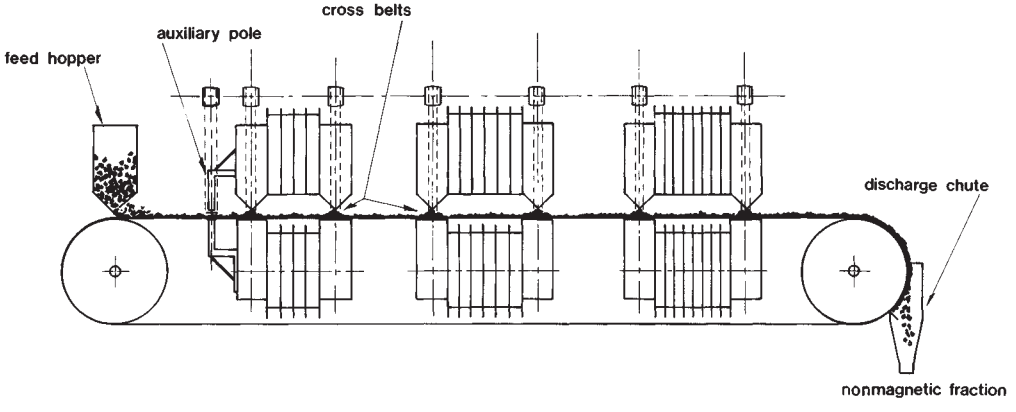


FIG. 19-42 Six-pole, seven-cross-belt magnetic separator. (*Courtesy of Readings, Inc.*)

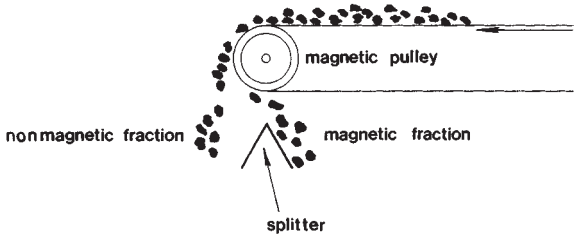


FIG. 19-43 Magnetic pulley.

magnetic disks. A schematic of an induced-roll separator is shown in Fig. 19-49. The best particle-size distribution for separation is minus 2 mm, plus 0.074 mm (minus 10 mesh, plus 200 mesh). Industrial devices are built with multiple rolls, which operate either in a series or in parallel, and can be used as concentrators or as purifiers (see Fig. 19-50). Standard widths for the rolls are 0.25, 0.5, and 0.75 m. Capacities vary between 1.5 and 18 t/(h·m). Induced-roll separators are used only to process weakly magnetic materials. **Capital costs** for this type of device are relatively low compared with those of other high-intensity magnetic separators, but **total process costs** are high owing to moisture-free feed requirements. A wet-process induced-roll separator was developed in the U.S.S.R. during the early 1960s and is reported to have a capacity of up to 100 t/h. In 1964 an Australian manufacturer introduced a wet-type induced-roll separator designed with a laminated, grooved rotor that rotates around a vertical axis (pole). These devices are built with up to 10 poles and are used principally to concentrate ilmenite sands. Capacity is approximately 0.8 t/h per magnetic pole.

Separations similar to those obtained with dry induced-roll devices can be obtained with cross-belt separators (Fig. 19-42). These units are built with up to eight poles, each of which can operate at different magnetic-field intensities to allow simultaneous production of different concentrates. However, capacity is low, and installed costs per ton capacity are high compared with induced-roll units.

Induced-Pole Separators In devices of this type, magnetic-field gradients are produced by the application of background magnetic field to a ferromagnetic matrix, thereby inducing magnetic poles around matrix edges. The correlation of edge and field directions

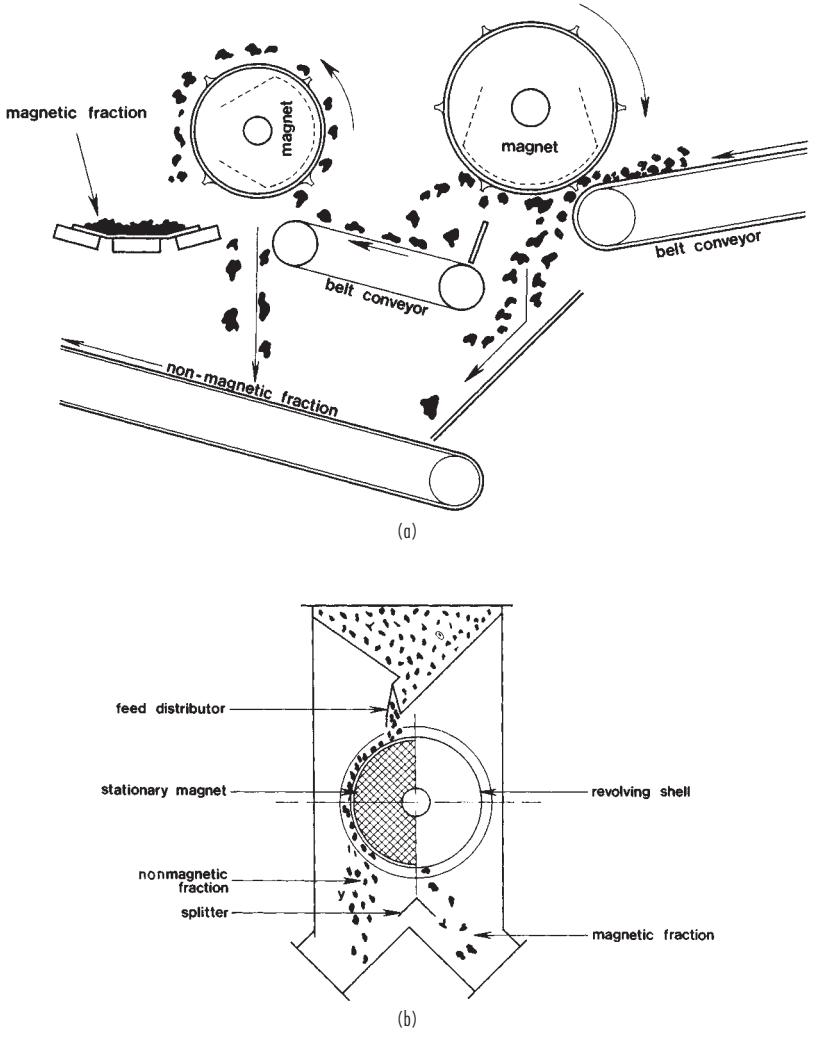


FIG. 19-44 Arrangement of magnetic drum separators. (*a*) Magnetic drum operating as a lifting magnet. (*b*) Magnetic drum operating as a pulley. (*Adapted from design courtesy of Eriez Magnetics.*)

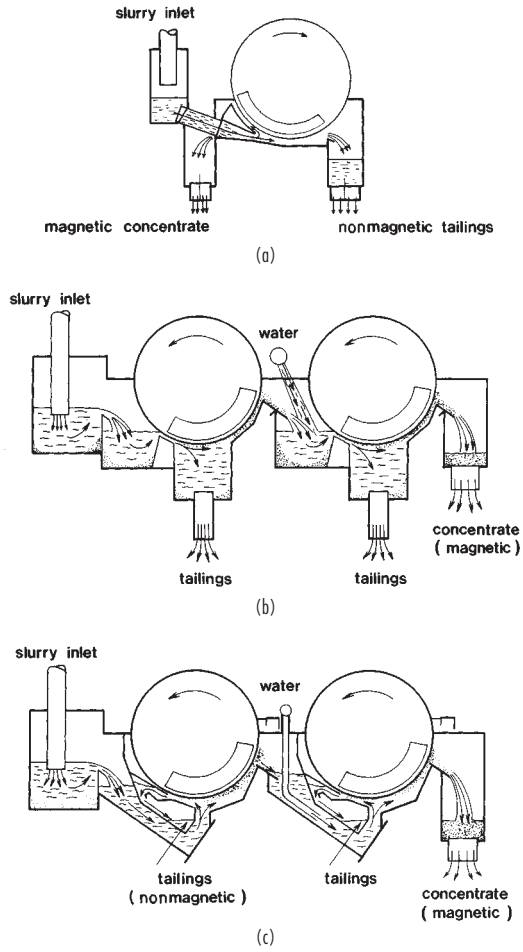


FIG. 19-45 Wet-drum-magnetic-separator arrangements. (*a*) Counterrotation-type wet magnetic drum separator. (*Courtesy of Sala International, Inc.*) (*b*) Concurrent-type wet magnetic double-drum separator. (*c*) Countercurrent-type wet magnetic double-drum separator.

determines whether the separator is a parallel field-to-flow unit or a perpendicular field-to-flow unit. In this category there are only two practical types of separator constructions, C-frame and solenoid. Uniformity of background magnetic field depends on design.

1. *C-frame magnets.* As shown in Fig. 19-38*b,* these magnets employ a ferromagnetic matrix placed between the poles of an electromagnet. With this design, however, the background magnetic field is not uniform. Also, high-magnetic-fringe fields are usually noticed in the flush region of these separators, and these can cause possible matrix clogging when even relatively small amounts of ferromagnetic particles are present in the slurry. The ferromagnetic material used to transfer the magnetic-flux lines from pole to pole occupies between 40 and 80 percent of the magnetized volume.

2. *Solenoid magnets.* These devices can be designed for wet or dry feeds. Depending on design, they can have a relatively uniform background magnetic field. It can be noted from Fig. 19-51 that the use of the return frame is important for generating a uniform mag-

TABLE 19-18 Maximum Depth of Material for Separator by Magnetic Pulley Based on Pulley Diameter and Linear-Velocity Belt

Diameter of pulley, mm	Belt linear velocity, m/s	Depth of mterial, mm
203	0.584	38
305	0.890	70
380	1.017	89
508	1.271	121
610	1.448	140
762	1.678	165
914	1.855	191
1067	2.033	210
1219	2.211	235

TABLE 19-19 Maximum Capacity for Magnetic Pulley Separator*

Pulley diameter, mm	Belt width, mm	Belt velocity, m/s	Capacity, m^3/h
	203		12.2
203	406	0.585	24.9
	610		62.3
	914		133.0
	305		38.0
	406		50.0
381	610	1.017	113.0
	914		255.0
	1219		515.0
	305		47.0
	406		59.0
457	610	1.143	130.0
	914		300.0
	1219		623.0
	406		88.0
	610		170.0
610	914	1.448	374.0
	1219		755.0
	1524		1133.0
	457		153.0
	610		218.0
914	914	1.855	481.0
	1219		935.0
	1529		1500.0

*Courtesy of Eriez Magnetics.

TABLE 19-20 Correction Factors for Magnetic-Pulley Capacities*

Type of application	Type of tramp iron to be removed	Correction factor
Crusher and primary-mill protection	Large and medium, over 30 g (1 oz)	1.0
Secondary-mill, pulverizer, and general separation	Large, over 30 g	1.0
	Medium, 30 to 240 g	1.3
	Small, 8 mesh (2.38 mm) to 30 g	2.0
Product purification	Fine ferrous contamination; finer than 8 mesh (2.38 mm)	4.0

*Courtesy of Eriez Magnetics.

TABLE 19-21 Influence of Magnetic-Drum Diameter on Separation*

Separator diameter, m	No. of stages	Composition of concentrates		Fe recovery, %	Feed rate, t/(h·m)
		SiO_2, %	Fe, %		
0.600	6	1.1–1.3	70.0	92	10–12
0.916	6	0.9–1.0	70.0	98	28–33
1.200	4	0.9–1.0	70.0	98	62–85

*Courtesy of Sala International Inc.

TABLE 19-22 Influence of Drum Diameter and Grind on Separator Capability*

Feed			Recommended capacities, t/(h·m)		
			Diameter of drum, m		
Description	Percent of feed minus 74 μm	Separator arrangement	0.60	0.90	1.20
Coarse	15–25	Concurrent	15–25	70–90	120–160
Medium	50	Concurrent or full countercurrent	10–15	35–50	60–90
Fine	75–95	Semicountercurrent	6–10	30–50	60–90

*Courtesy of Sala International Inc.

netic field. Filamentary-type matrices, which occupy less than 10 percent of the magnetized volume yet still provide very high field gradients, can be used with these types of magnets.

The most familiar of the C-frame, matrix-type industrial magnetic separators are the Carpco, Eriez, Readings, and Jones devices. The Carpco separator employs steel balls as a matrix, Eriez uses a combination of expanded metal matrices, and the Readings and Jones separators have grooved-plate matrices. Capacities for this type of unit are reported to up to 180 t/h (in the case of Brazilian-hematite processing).

Solenoid magnetic separators are designed for batch-type, cyclic, and continuous operation. Devices which can use matrices of expanded metal, grooved plates, steel balls, or filamentary metals have been designed. Continuous separators with capacities to 600 t/h for iron ores (similar to the Brazilian hematite) are commercially available (Sala International Inc.). Selection of the method of operation is application-dependent, being based on variables such as temperature, pressure, volume of magnetics in the feed, etc.

A familiar type of cyclically operated solenoid electromagnet is the Franz separator, a well-known continuous type of solenoid separator manufactured by Krupp-Sol. An enclosed flux return-frame solenoid design for cyclic and continuous use is built by Sala International Inc.

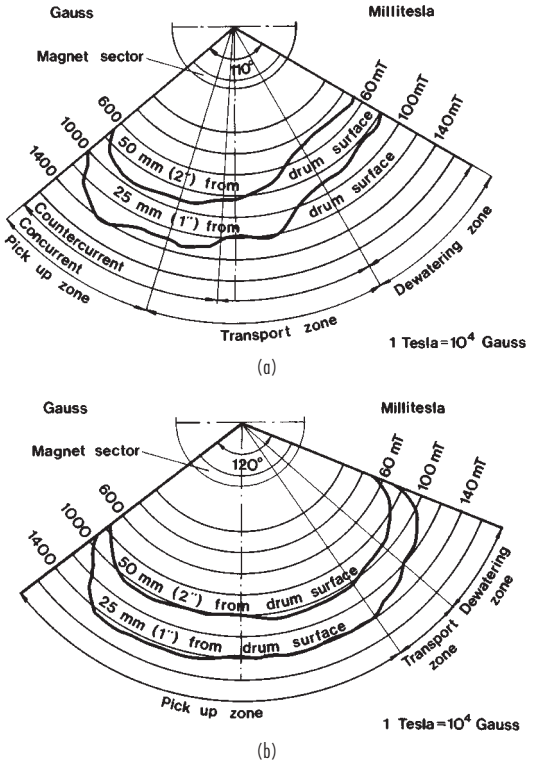


FIG. 19-46 Magnetic-field distribution charts. (*a*) Concurrent and countercurrent wet drum magnetic separator, 1.2-m diameter. (*b*) Counterrotation wet drum magnetic separator, 1.2-m diameter. (*Courtesy of Sala International, Inc.*)

A schematic of a continuous Sala high-gradient magnetic separator is shown in Fig. 19-52.

Depending on the type of matrix used, induced-pole magnetic separators can be classified as either high-intensity magnetic separators, which utilize grooved plates or steel balls as the matrix material, or as high-gradient magnetic separators, which use filamentary matrices such as steel wool or expanded metal. Filamentary matrices have proved to be more advantageous.

The maximum magnetic field produced by a C-type device is 2 T. For solenoids, conventional designs produce magnetic-field intensi-

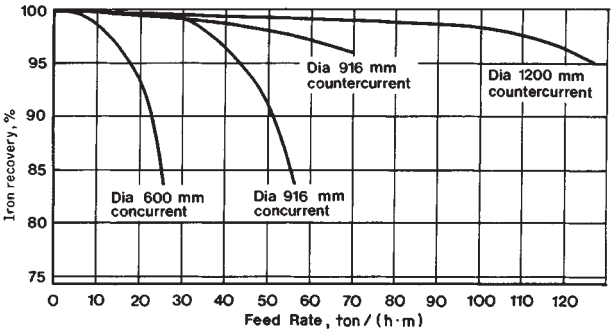


FIG. 19-47 Influence of drum diameter on separation. (*Courtesy of Sala International, Inc.*)

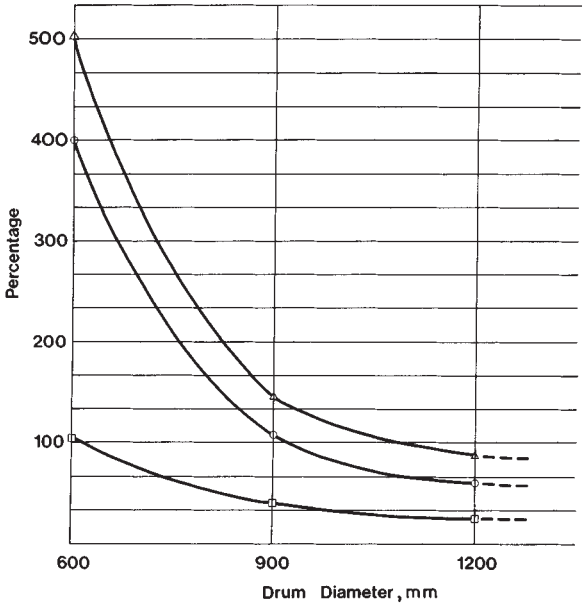


FIG. 19-48 Influence of drum diameter on separation cost. △, Two stages coarse separation; ○, three stages fine separation; □, sum of coarse and fine separations. (*Courtesy of Sala International, Inc.*)

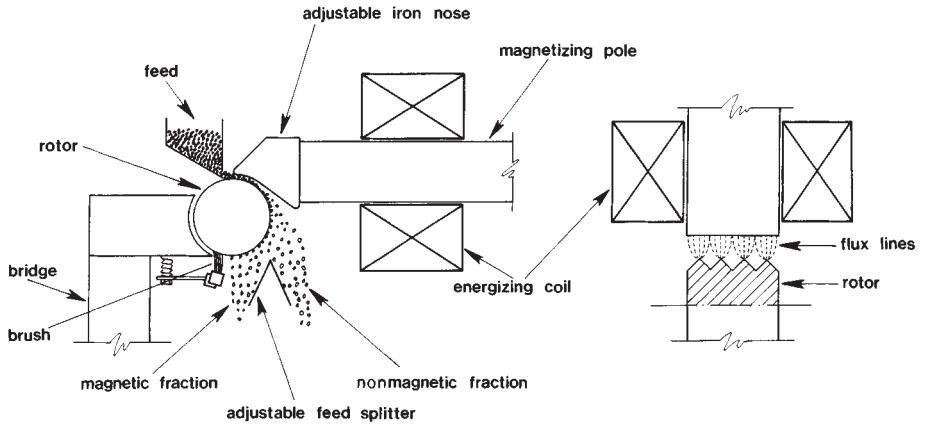


FIG. 19-49 Schematic diagram of an induced-roll separator.

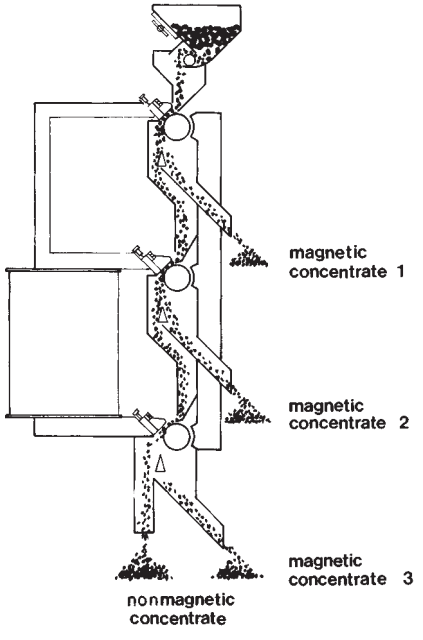


FIG. 19-50 Multiple induced-roll magnetic separator.

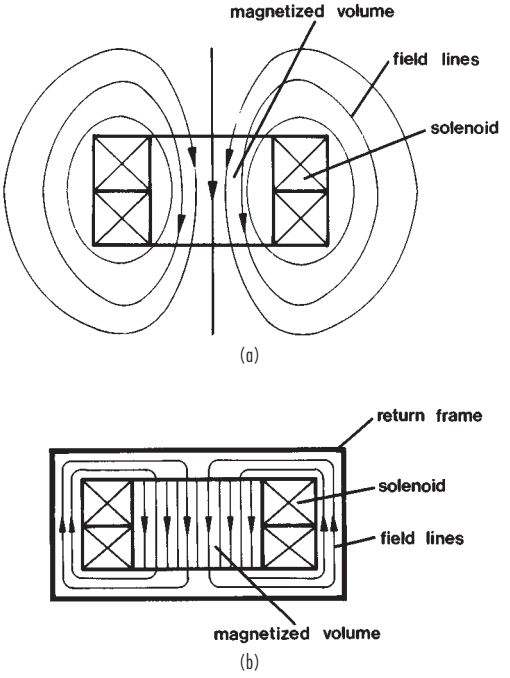


FIG. 19-51 Solenoid-type magnets. (*a*) Nonuniform field. (*b*) Uniform field by use of return frame.

ties up to 2 T, while superconducting units can be constructed with ratings up to 8 T.

In all induced-pole devices, the more magnetic particles are retained on the matrix while the less magnetic fraction is carried away in the slurry.

Dynamic (or Deflecting) Devices The oldest type of dynamic separation device is the Franz Isodynamic separator. This laboratory device has a dipole configuration with the poles shaped so that the value of $H\ dB/dz$ is constant throughout the working separation volume. Material to be separated can be fed through a vibratory chute or dropped between the poles, producing a separation based only on relative magnetic susceptibility.

There are a variety of new developments in magnetic separation which are of possible interest, but their commercial applicability is still not yet assured. These include quadripole separators and a spiral-flow device.

Table 19-23 lists potential applications for all types of magnetic separators.

SUPERCONDUCTING MAGNETIC SEPARATION

Superconducting Magnets In a superconducting magnet the magnetic field is generated in exactly the same way as on a normal electrical solenoid, coil, or winding. The only real difference is that the conductor is made from superconducting alloy which has to be maintained at a suitably low temperature to maintain the superconducting state. There are a number of possible material compositions which can be used for the superconducting winding but for industrial applications where economics and reliability play a key role an alloy of niobium and titanium is presently the preferred choice.

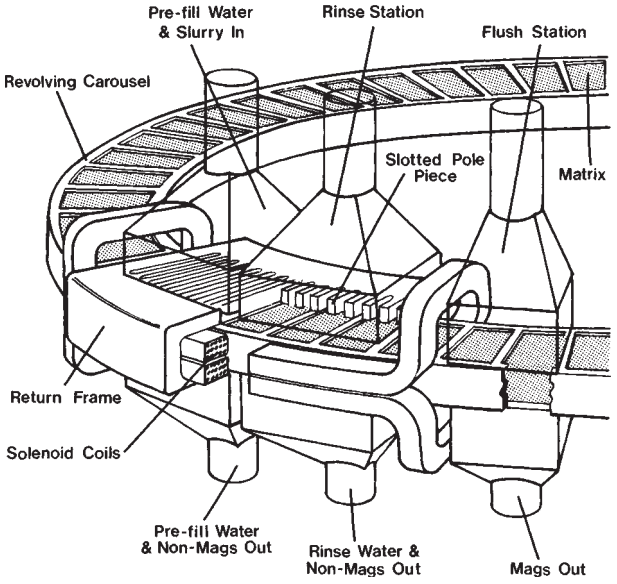


FIG. 19-52 Schematic of continuous high-gradient magnetic separator. (*Courtesy of Sala International, Inc.*)

Superconducting windings of N6Ti are now so commonplace that they can be considered as conventional superconductors. What is more relevant to the construction of a superconducting magnetic separator is the choice of refrigeration or cryogenic system used to cool the magnet winding, and it is the cryogenic system which to a large extent dictates the economics and practicality of these machines. There are presently three cryogenic routes which have been successfully applied.

1. *Closed-cycle liquefier systems.* In this design the superconductor resides in a bath of liquid helium and boil-off gas is recirculated through a helium liquefier. The installation of such a system is quite complex but these installations have proved good reliability providing there are no long-term interruptions to the supply of electrical power and cooling water.

2. *Low-loss system.* In a low-loss system the winding also resides in a reservoir of liquid helium but a very efficient insulation system enables the magnet to operate for long periods, typically 1 year or more, between liquid helium refills. An important feature of these systems is that they are relatively immune to short-term electrical power failures, which has enabled complete reliability even in extremely difficult environments.

3. *Indirect cooling.* The advent of heat engines based on the Gifford McMahon cycle to generate temperatures of 4 kelvin or less has made it possible to cool superconducting windings without the need for liquid helium. This technique offers great potential for small-scale systems where the economics of helium supply or the cost of a liquefier cannot be justified. The only drawback is that a constant supply of electrical power is essential for reliable operation.

The key benefits offered by superconducting magnets are (1) very low power consumption resulting from zero resistance of the magnet winding and (2) much higher magnetic fields which can be generated.

Superconducting magnets are presently being used in two distinct types of devices: *high-gradient magnetic separators* (HGMS) and *open-gradient magnetic separators* (OGMS). We shall consider these in turn.

Superconducting HGMS The HGMS principle relies on the capture of magnetic particles on a magnetized ferromagnetic matrix, as described in previous sections. In this type of device where an increase in magnetic-field induction enables capture of weaker magnetics and power consumption of large-scale systems is an important economic factor it is not surprising that superconducting magnets have made a significant impact. Indeed, for large-scale HGMS, superconducting magnets are by far the preferred choice.

A key feature of the HGMS process is that periodically the matrix must be demagnetized to flush out the captured magnetics. For superconducting magnets this demagnetization can be achieved by either de-energizing the magnet (switched-mode HGMS) or by moving the matrix canister (referred to as reciprocating canister HGMS) out of the magnetic field. The reciprocating matrix canister method is unique to superconducting HGMS and is shown schematically in Fig. 19-53. The differences resulting from the superconducting and resistive electromagnet HGMS systems are quite evident from the engineering data shown in Table 19-24.

TABLE 19-23 Potential Applications of Magnetic Separators

Device type	Type of construction	Maximum background magnetic field, Oe	Type of matrix which can be used	Maximum field gradient obtainable, G/cm	Required magnetic susceptibility for particulates	Particle size to be treated, mm	Materials which can be treated; fields of use
Grate	Permanent magnet	500	Rods	500	Ferro	<12	Tramp and fine iron
Pulley	Permanent magnet and electromagnet	100–200	—	100–1000	Ferro, strongly	<50	Ferro and strongly magnetic
Belt	Electromagnet	100–1000	—	100–1000	Strongly	0.15–30	Strongly magnetic
Drum	Permanent magnet and electromagnet	500–1000	—	500–1000	Strongly	0.02–20	Magnetite processing
Franz Isodynamic	Electromagnet	10,000	—	2000	Strongly, weakly	>0.01	Only for laboratory
Solenoid; Franz ferrofilter	Electromagnet	20,000	Steel ribbons, balls	200,000	Strongly, weakly	>0.01	Tramp and fine iron, ceramic slurries, industrial minerals, chemical industry
Induced rolls	Electromagnet	20,000	—	200,000	Strongly	0.03–3	Dry, dedusted, weakly magnetic particles
C-frame type; Jones	Electromagnet	20,000	Grooved plates	200,000	Strongly, weakly	0.01–2	Iron ores, industrial minerals
Carpco	Electromagnet	20,000	Steel balls	45,000	Weakly	0.01–1	Iron ores, industrial minerals
Marston Sala high-gradient magnetic separator	Electromagnet, superconducting	20,000 50,000	Steel wool, expanded metal, steel balls	25×10^6	Strongly to very weakly	0.0001–2	Iron ores, industrial minerals, coal, liquefied coal, wastewaters, purifiers, catalyst recovery, chemical industry

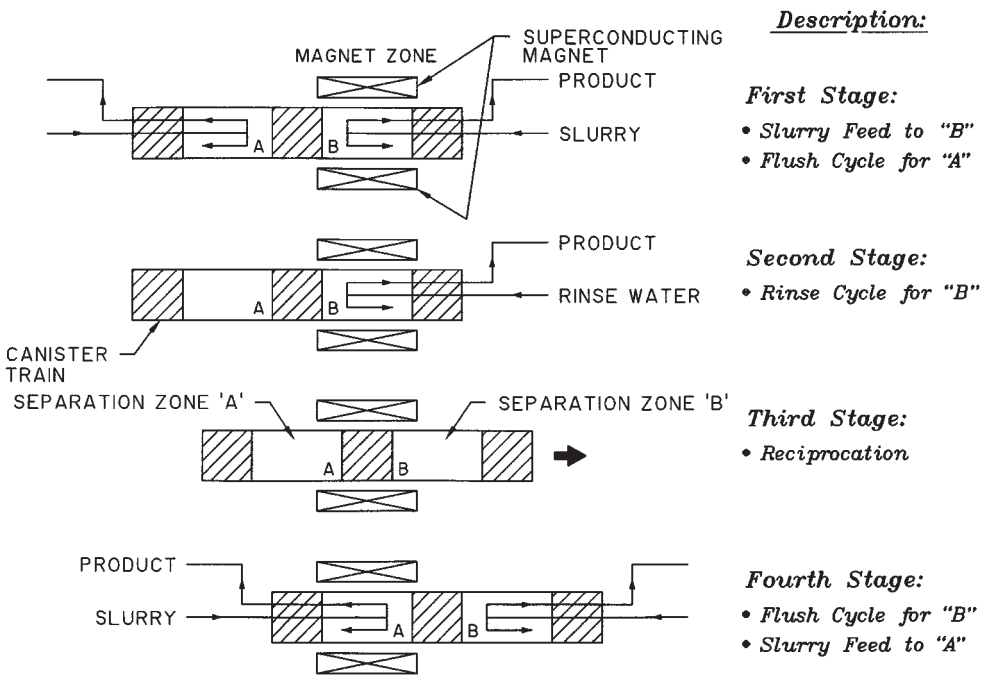


FIG. 19-53 Basic process cycle for a reciprocating canister superconducting magnetic separator. (*Courtesy Carpco, Inc.*)

One might expect that the perceived complexities of superconducting magnets would restrict their use to highly developed and industrialized areas. It is therefore noteworthy that the simplicity and reliability of the combination of low-loss cryogen technology coupled with the reciprocating canister principle has enabled a number of these HGMS units to operate with total reliability in areas as remote as the Amazon rain forest areas of Munguba and Rio Capim. Figure 19-54 shows the installation of a typical large-scale reciprocating canister HGMS.

A new development which shows promise of imminent industrial application is superconducting HGMS designed for treating dry feeds. One such unit employing a vibrating matrix in a reciprocating canister design has been evaluated with promising results. Once again the advantages of low power consumption and significantly improved levels of beneficiation are the key factors in driving this technology into industry.

Superconducting OGMS In open-gradient magnetic separators (OGMS) the magnet structure is arranged to provide a region in open space with a highly divergent field. Thus, the magnet geometry provides both the magnetic field and field gradient. Any paramagnetic material passing through this region will experience a force directly proportional to the field intensity and magnitude of field gradient. There are many conventional devices ranging from lift magnets to rare earth-drum and roll-type separators that operate on this principle. Superconducting OGMS has the benefit of offering not just higher magnetic force profiles, but a significantly greater depth of reach (i.e., larger separation volume) than permanent magnet and electromagnet devices. All superconducting OGMS units at the present operate with dry feeds usually with particle size >75 μm.

The earliest industrial application of superconducting OGMS was based on a drum separator design referred to as the "desces" separator. The drum was 1 meter in diameter and generated a peak field of 3 tesla and field gradient of 40 tesla/meter. A helium re-liquefier was required to provide adequate cryogenic capacity which significantly affected the capital cost, nevertheless, the unit has been operated successfully for many years in the beneficiation of magnesite processing normally 150 mm material at feed rates of up to 100 TPH.

A somewhat simpler and more compact OGMS device referred to as the "Cryostream" has recently been introduced. This unit operates on the inclined-fall process in which the magnet is held at an incline and material is simply allowed to fall through the magnetic region. The treatment size for the Cryofilter is 25 × 0.5 mm. The winding structure and overall geometry of this system make it an ideal candidate for indirect cooling by providing both overall simplicity and economic benefits.

TABLE 19-24 Comparative Data for 50 TPH HGMS Plant

	Superconducting Cryofilter 5T/460	Switched-mode superconducting HGMS	Conventional electromagnet
Magnetic induction	5 tesla	2 tesla	2 tesla
Separator weight	45 tons	250 tons	300–400 tons
Operator power consumption	10 kW	40–80 kW	280–400 kW
Overhead service crane for matrix canister exchange	2 tonne rail mounted	15 tonne gantry	15 tonne gantry
External cryogenic requirements	None required	1. Helium liquefier 2. Helium compressor 3. Liquid helium storage tank 4. Liquid nitrogen storage tank 5. Helium gas ballast tank	Not applicable



FIG. 19-54 Superconducting magnetic separator operating in a kaolin treatment plant. (*Courtesy Carpco, Inc.*)

The Cryostream operates with a peak field of 4 tesla and a magnetic force of 250 T^2/m allows separation of minerals with magnetic susceptibilities in the order of 10^6 emu/g. In essence the Cryostream is an industrial-scale version of the well known laboratory Frantz Isodynamic Separator.

ELECTROSTATIC SEPARATION

GENERAL REFERENCES: *SME Mineral Processing Handbook,* Society of Mining Engineers of the AIMMPE, NY, 1985 Edition. Moore, *Electrostatics and Its Applications,* Wiley-Interscience, New York, 1973. Knoll, Taylor, *Advances in Electrostatic Separation,* Minerals & Metallurgical Processing, 1985. E. Tondu et al., *Commercial Separation of Unburned Carbon from Fly Ash,* Mining Engineering, June 1996, p. 47–50.

General Principles Electrostatic separation (of particles), also commonly known as high-tension separation, is a method of separation based on the differential attraction or repulsion of charged particles under the influence of an electrical field. Applying an electrostatic charge to the particles is a necessary step before particle separation can be accomplished. Various techniques can be used for charging. These include contact electrification, conductive induction, and ion bombardment.

Regardless of the method of charging, the amount of charge that can be accumulated on a particle is limited by the maximum achievable charge density and the surface area of the particle. Electrostatic separation of mixed particles is possible when the electrostatic force acting on some particles is great enough to overcome gravity or inertial forces. Because the surface area of a solid varies as the square of a linear dimension whereas the mass varies as the cube of that dimension, gravity and inertial forces acting on solid particles increase faster with particle size than do electrostatic forces for charged particles in electric fields. Thus, there are upper size limits beyond which electrostatic separation of particles of a given shape is not feasible. For granular materials, this upper size limit is about 4 mm; for thin pieces of large cross-sectional area and for long pieces of small cross-sectional area, the limit can be greater than 25 mm.

The motion of fine particles immersed in a moving fluid is more greatly affected by fluid drag forces than that for similar large particles. For very small particles in a fluid, particle motion approximates the motion of the enveloping fluid. Industrial electrostatic separation of solid particles, which is universally conducted in air (or other easily ionizable gas), is difficult at particle sizes less than about 0.074 mm (200 mesh).

Charging Mechanisms

***Contact Electrification* (Fig. 19-55*a*)** When dissimilar materials touch each other, there is an opportunity for the transfer of electric charges. The extent of charge transfer can be such that a significant surface charge of opposite sign is developed when the materials are

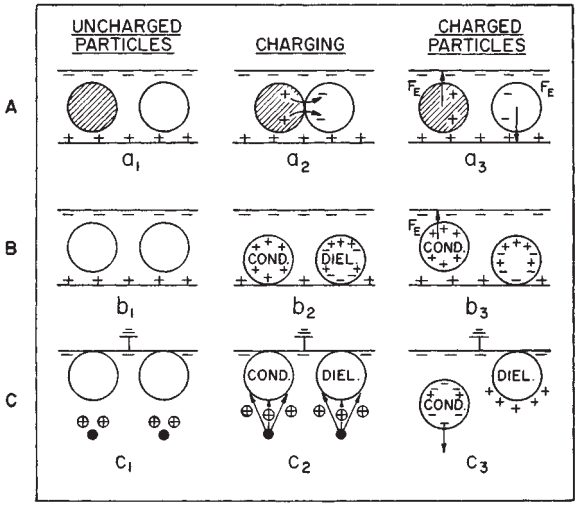


FIG. 19-55 Schematic representation of charging mechanisms. (*A*) Contact electrification. (*B*) Conductive induction. (*C*) Ion bombardment. Cond. = conductor particle; diel. = dielectric particle; ● = high-voltage dc electrode; ⊕ = ions from corona discharge at high-voltage electrode.

later separated. High temperatures and low humidity favor the development of high surface charges through the mechanism of contact electrification. Rubbing the materials together to increase the area of effective contact can also lead to high surface charges.

Particles carrying charges of opposite polarity due to contact electrification will be attracted to opposite electrodes when passing through an electric field and thus can be separated from each other.

***Conductive Induction* (Fig. 19-55*b*)** The term *conductive induction* describes the process by which an initially uncharged particle that comes into contact with a charged surface assumes the polarity and, eventually, the potential of the surface. A particle that is an electrical conductor will assume the polarity and potential of the charged surface very rapidly. However, a nonconducting particle will become polarized so that the side of the particle away from the charged surface develops the same polarity as the surface. Particles of intermediate conductivity may be initially polarized but approach the potential of the charged surface at a rate depending on their conductivity.

If a conductor particle and a nonconductor particle are just separated from contact with a charged plate, the conductor particle will be repelled by the charged plate and the nonconducting particle will be neither repelled nor attracted by it.

The charged plate must be balanced by other oppositely charged (or earthed) bodies to maintain overall neutrality. In electrostatic separation, this is usually accomplished by means of a single electrode of charge opposite in sign to that of the charged plate. The conductor particle is then in the electrical field between the two electrodes and experiences a net electrostatic force in the direction of the second electrode. The nonconducting particle, having no net charge, experiences no electrostatic force in a uniform electric field. Electrostatic separation of the conductor and nonconductor particles can be accomplished by movement of the conductors in the electric field.

***Ion Bombardment* (Fig. 19-55*c*)** The most positive and strongest method of charging particles for electrostatic separation is ion bombardment. Use of ion bombardment in charging materials of dissimilar properties may be visualized by considering conductor and nonconductor particles touching the grounded conducting surface of Fig. 19-55*c*. Both particles are bombarded by ions of atmospheric gases generated by an electrical corona discharge from a high-voltage electrode (usually a fine tungsten-alloy wire at 20 to 30 kV with respect to ground and several centimeters away from the particles). When ion bombardment ceases, the conductor particle loses its acquired charge to ground very rapidly and experiences an opposite electrostatic force tending to repel it from the conducting surface. The nonconducting particle, however, being coated on its side away from the conducting surface with ions of charge opposite in electrical polarity to that of the surface, experiences an electrostatic force tending to hold it to the surface. If the electrostatic force is larger than the force of gravity or other forces tending to separate the nonconducting particle from the conducting surface, the particle is held in contact with the surface and is said to be "pinned."

Electrostatic-Separation Machines The first electrostatic machines to be used commercially employed the principle of contact electrification. These were free-fall devices incorporating large vertical plates between which an electrostatic field was maintained. Triboelectric separation (contact charging) has experienced an increase in applications due to advances in mechanical self-cleaning and electrical design as well as the development of efficient precharging techniques.

Triboelectric Separators There are currently two industrial forms of triboelectric separators installed commercially to treat minerals and recycled plastics:

Tube-type. These separators are typically divided into two sections: (1) precharging and (2) separation. The precharging section is designed to create or enhance the charge difference between particles to be separated (typically by some form of contact mechanism or external pretreatment to render one constituent positive or negative in comparison to the other materials present. The separation section consists of two vertical walls of tubes opposing each other. Each tube

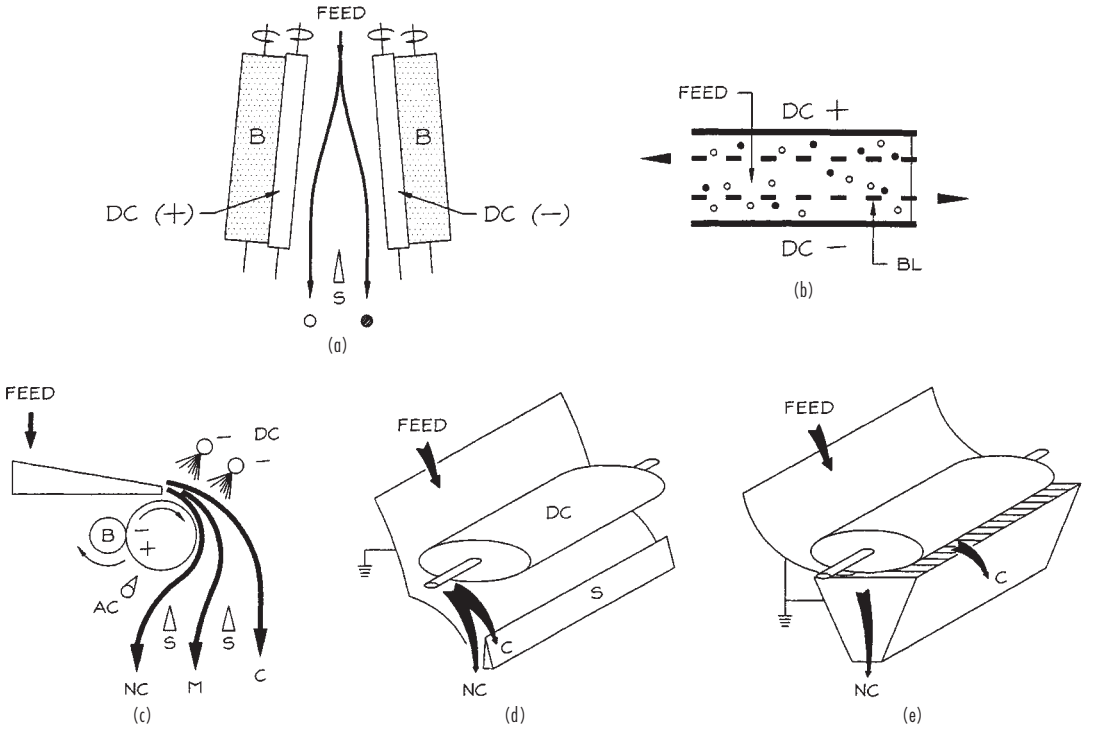


FIG. 19-56 Operating principles of electrostatic separators. *C* = conductors; *NC* = nonconductors; *M* = middling; *DC* = high-voltage dc electrodes; *AC* = high-voltage ac wiper (electrodes); *B* = brush; *S* = splitter; ○ = negatively charged particles; ● = positively charged particles; *BL* = belt.

"wall" is electrified with the opposite potential, and product splitters running parallel to the electrode walls at the base of unit separate materials attracted to the oppositely charged tube electrodes. This arrangement is illustrated in Fig. 19-57.

Belt-type. Figure 19-58 illustrates a horizontal belt-type separator equipped with fast-moving belts that travel in opposite directions adjacent to suitably placed plate electrodes of the opposite polarity. Material is fed into a thin gap between two parallel electrodes. The particles are swept upward by a moving open-mesh belt and conveyed in opposite directions, thus facilitating particle charging by contact with other particles. The electric field attracts particles up or down depending on their charge. The moving belts transport the particles adjacent to each electrode toward opposite ends of the separator.

The common types of other industrial electrostatic separators employ charging by conductive induction and/or ion bombardment. Figure 19-56 illustrates the principles of application.

Conductive-Induction Machines Electrostatic separators exploiting the principle of conductive induction will generally use the following electrode designs:

Plate separators. These separators introduce material typically by gravity onto a grounded-metal slide in front of which is placed a static electrode of large surface area. The elaborate contact electrification used in earlier free-fall electrostatic separators was avoided in later devices by incorporating the slide principle. Separation occurs by particles selectively acquiring an induced charge from the grounded plate and then being attracted in the direction of the charged electrode. Refer to Fig. 19-59.

Screen-plate separators. These include a metal slide at ground potential that is extended with a conducting screen of suitable screen-opening size to allow easy passage of the largest grains being treated. A stationary electrode is placed above the slide and screen sections as shown in Fig. 19-56*e*. Particles capable of assuming an induced charge from the slide are attracted by the electrode and prevented from passing through the screen grid; the other particles pass through the screen unaffected.



FIG. 19-57 Triboelectric separators. V-Stat electrostatic separator for silica removal from industrial minerals. (*Courtesy of Carpco, Inc.*)

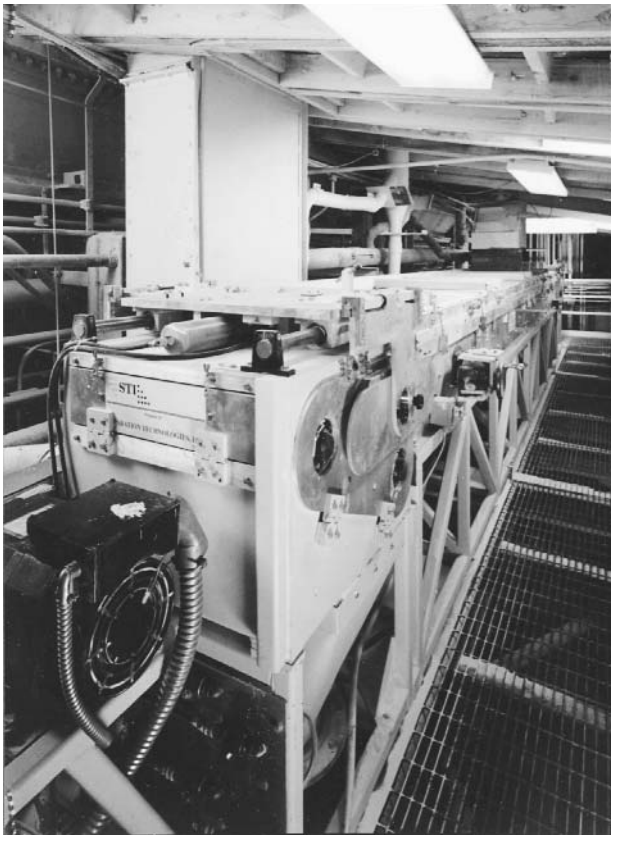


FIG. 19-58 Triboelectric separators. Belt-type electrostatic separator for separation of carbon from fly ash. (*Courtesy of Separation Technologies, Inc.*)

Ion-Bombardment Machines *Conductive roll (drum) separators.* These separators are, by far, the most widely employed industrial-machine type. The electrostatic elements of these machines consist of a conductive rotating drum at ground potential coupled with one or more high-voltage ionizing electrodes. Suitably placed nondischarging (static) electrodes are often used in conjunction with an ionizing electrode to create a static field which aids centrifugal force in removing conductive particles from the drum surface.

Drum construction is typically of carbon or stainless steel when treating granular materials minus 1 mm in size. Drum diameter has ranged from 0.150 to 0.360 m, while drum length varies from 0.460 to 3.050 m in industrial ion-bombardment (high-tension) machines.

Feeding these separators is accomplished by vibratory, belt, rotary spline, or gravity methods, depending on the particle size being treated. Vibratory and belt feeding techniques are preferred for coarser sizes, and rotary spline and gravity methods are normally used for finer materials. Exceptions to this generalization can be observed in plant practice. The ionizing electrodes employed in these machines vary considerably in appearance, but all produce a corona.

An alternating-current electrode system referred to in the industry as a "wiper" is often installed in the nonconductor product-collection section behind each drum. The function of the wiper is to use an ac corona to neutralize the charge on the nonconductor particles pinned

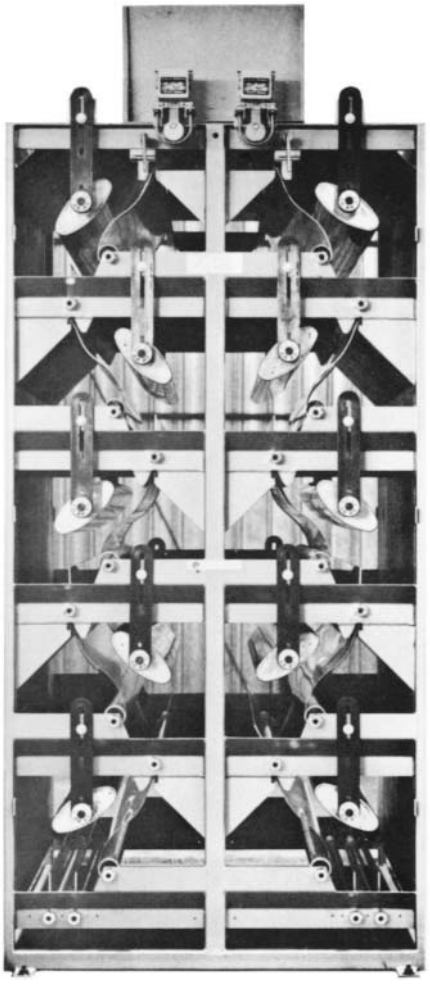


FIG. 19-59 Conductive-induction plate-type electrostatic separator. (*Courtesy of Mineral Technology, Ltd.*)

to the surface of the drum and thereby reduce the workload for mechanically operated brushing systems.

Ion-bombardment machines are available in horizontal and vertical (stacked) configurations. Horizontal units are preferred for large-tonnage applications in which machines are arranged in rows for ease of maintenance and operation. Stacked units up to four rolls high have been used to reduce material-handling costs in multipass treatment schemes when the material is capable of being passed vertically from one roll to another by gravity. Internal details of industrial roll-type separators are shown in Fig. 19-60.

Power Supplies High-voltage ac and dc power supplies for electrostatic separators are usually of solid-state construction and feature variable outputs ranging from 0 to 30,000 V for ac wiper transformers to 0 to 60,000 for the dc supply. The maximum current requirement is approximately 1.0 to 1.5 mA/m of electrode length. Power supplies for industrial separators are typically oil-insulated, but smaller dry-epoxy-insulated supplies are also available.

Features common to most high-voltage dc power supplies include reversible polarity, short-circuit and current-limiting protection, and automatic residual-charge dissipation to ground.



FIG. 19-60 Internal configuration of roll-type electrostatic separator, ionizing mode. (*Courtesy Carpco, Inc.*)

High-voltage controllers which regulate primary input voltage to the rectifier and wiper transformer and house primary current-limiting protection, meters, and instrumentation are designed for local or remote operation.

Machine Capacities Table 19-25 presents machine-capacity information for electrostatic separators.

Applications of Electrostatic Separation

Mineral Beneficiation Electrostatic methods are widely used in the processing of ores with mineral concentrates. Generally, electrostatic separation is used as a part of an overall flow sheet comprising various combinations of physical separation procedures. It is particularly well established in the processing of heavy-mineral beach sands from which are recovered ilmenite, rutile, zircon, monazite, silicates, and quartz. High-grade specular hematite concentrates have been recovered at rates of 1000 tons/h in Labrador. Applications also include processing tin ores to separate cassiterite from columbite and ilmenite. Refer to Fig. 19-61*a*.

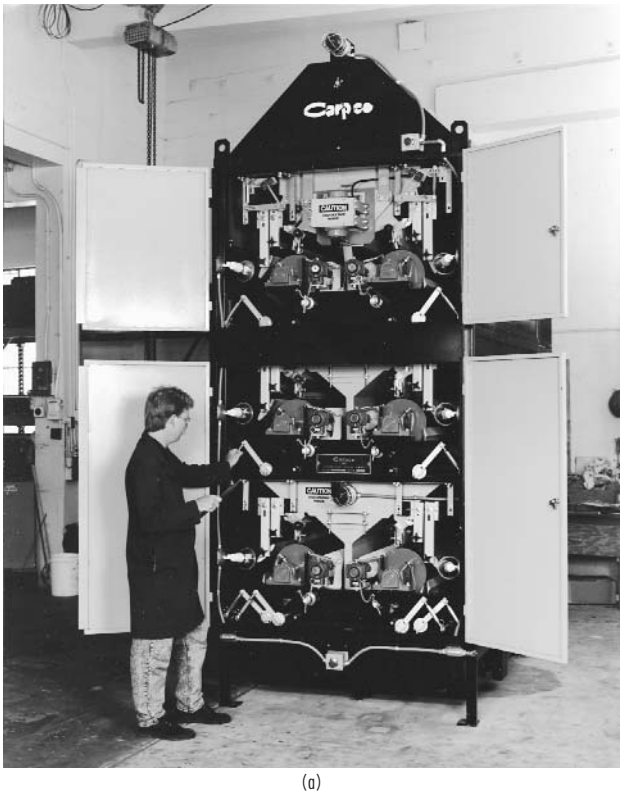
Charging by ion bombardment is the technique used in most mineral separations. The conductive-induction (nonionizing) plate types of separators have also been used. Applications of this device in the minerals industry include its use as a final cleaning step when concentrating rutile and zircon.

Generally, separators of the conductive-induction type have a lower capacity per unit length of electrode than the ion-bombardment (ionizing) type of apparatus, and multipass operation is typically required. This disadvantage is offset by the ability of these separators to (1) produce high-grade concentrates from ore materials that are otherwise difficult to process and (2) process a coarser material than competitive

TABLE 19-25 Machine Capacities of Electrostatic Separators for Mineral Applications

Type	Capacity, t/h
A) Triboelectric separators	
• Belt type (1 pass)	10
• Tube type (1 pass)	20
B) Conductive-induction electrostatic separators Plate separator: basis, 5 pass × 2 start; 1.42 m in length per start; capacity, 900 kg/(h·m)	2.0
C) Ion-bombardment electrostatic separators 2-m units-basis:	
• 1 pass × 6 starts × 2 m × 2000 kg/(h·m)	24
• 3 pass × 2 start × 2 m	8

NOTE: Capacity information is based on the treatment of industrial minerals having a specific gravity of 2.6 to 4.0.



(a)



(b)

FIG. 19-61 (*a*) Mineral separation: high-capacity 4-roll (250 mm dia × 2000 mm long) separator featuring all-start × 2-pass separation. Siz-roll units also available. (*b*) Recycling separator for nonferrous metals and plastics: 4-roll (350 mm dia × 1500 mm long) separator featuring 2-start × 2-pass or 1-start × 4-pass separation. (*Courtesy Carpco, Inc.*)

processes such as froth flotation. These units are used as a final cleaning stage for rutile and zircon.

Electrostatic-type separation is being tested as an alternative to the presently used process of flotation of pebble phosphates for coarser-size fractions. Advantages sought include reduced reagent costs, a lower water requirement, and fewer tailings-disposal problems when a part of the flotation circuit is eliminated. The largest application of triboelectric separation is in the salt industry where sodium and potassium salts are separated after preconditioning.

Plastic and Metals Recycling Electrostatic separation has been increasingly applied to recover nonferrous metals from industrial plastics (telephone and communication scrap). It also is an important step in the recycling of beverage bottles to reject any remaining nonferrous metals. Both of these recycling applications make use of roll-type ion-bombardment separators (Fig. 19-61*b*).

A new application of triboelectric separation involves the separation of PVC from PET and other plastics. Recent developments in precharging technology permit PVC to assume a strong negative charge and be removed efficiently from properly protected mixed plastic feedstocks (Fig. 19-62).

Other Applications Electrostatic separators have been used to separate a number of different types of materials not only on the basis of differences in dielectric properties but also in combination with differences in surface conductivity and shape factors. Among these operations are seed sorting, cleaning of spices, separating of pill coatings from base materials, removal of textile from reclaimed plastics, and separation of paper and plastic. Electrostatic separation has also been adapted for use in classification and sizing when elongated particles or extremely fine sizes cause difficulty in conventional dry-screening applications.

Typical Operating Conditions Table 19-26 presents some typical values of important operating conditions for the separation of several different types of feed materials. In considering candidate processes for a given separation job, the table can sometimes be helpful in showing that materials of similar properties and/or economic value can be treated by electrostatic separation.



FIG. 19-62 New Triboelectric separator for separation of PVC from other plastics. (*Courtesy Carpco, Inc.*)

TABLE 19-26 Typical Operating Conditions for Electrostatic Separations

Type of particle charging	Feed	Separation	Type of separator	Feed temperature, °C	Feed size, mm	Feed rate, metric tons per hour per start*	No. of stages of separation
Triboelectric	Silica from limestone	Reduction of quartz by 80–90%	Tube type	80–100	–1.0 + 0.015	20	1
	Florida pebble-phosphate flotation conc.	Residual silica from pebble phosphate	Tube type	70–90	–1.0 + 0.10	10–15	1
Conductive induction	Zircon or rutile concentrate (eastern Australia)	Residual conductor minerals from rutile and zircon; upgrading of concentrate from 98.95 to 99.35% zircon at 92% recovery	Plate	50–80	–0.21 + 10.074	0.6–0.7	5–10
Ion bombardment	Heavy-mineral concentrate	Conductor minerals (ilmenite, rutile) from non-conductor minerals (zircon, monazite, aluminum silicates, quartz and others)	Roll	120	–1.0 + 0.04	2.5	3–6
	Iron ore	Iron oxides from quartz and silicates	Roll	120	–1.0	6–7	2–4
	Tungsten concentrate	Scheelite from iron oxides and other conductor minerals	Roll	150	–0.6	1.0–1.5	3
	Chrome ore	Chromite from silica and silicates	Roll	120	–0.85		
	Chopped wire	Metal from plastic insulation	Roll	Ambient	–12.5	1.5–2.0	2–4
	Metal powder	Removal of nonmetallic impurities	Roll	Ambient to 120	–0.20	1–2	2–4

*To convert metric tons per hour per start to kilograms per second per start, multiply by 0.2778.

FLOTATION

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INTRODUCTION

Mixed liberated particles can be separated from each other by flotation if there are sufficient differences in their wettability. The flotation process operates by preparing a water suspension of a mixture of relatively fine-sized particles (smaller than 150 micrometers) and by contacting the suspension with a swarm of air bubbles of air in a suitably designed process vessel. Particles that are readily wetted by water (hydrophilic) tend to remain in suspension, and those particles not wetted by water (hydrophobic) tend to be attached to air bubbles, levitate (float) to the top of the process vessel, and collect in a froth layer. Thus, differences in the surface chemical properties of the solids are the basis for separation by flotation.

Surfaces that do not have strong surface chemical bonds that were broken tend to be nonpolar and are not readily wetted. Substances such as graphite and talc are examples that can be broken along weakly bonded layer planes without rupturing strong chemical bonds. These solids are naturally floatable. Also, polymeric particles possess nonpolar surfaces and are naturally hydrophobic. By contrast, most naturally occurring materials are polar and exhibit high free energy at the polar surface. The polar surfaces react strongly with water and render those particles naturally hydrophilic. The relative wettability of the solids in a mixture can be enhanced by the addition of various surface chemical agents that are adsorbed selectively on the particle surface.

Mineral Applications. The flotation process is most widely used in the mineral process industry to concentrate mineral values in the ores.

A U.S. Bureau of Mines survey covering 202 froth flotation plants in the United States showed that 198 million tons of material were treated by flotation in 1960 to recover 20 million tons of concentrates which contained approximately $1 billion in recoverable products. Most of the world's copper, lead, zinc, molybdenum, and nickel are produced from ores that are concentrated first by flotation. In addition, flotation is commonly used for the recovery of fine coal and for the concentration of a wide range of mineral commodities including fluorspar, barite, glass sand, iron oxide, pyrite, manganese ore, clay, feldspar, mica, sponumene, bastnaesite, calcite, garnet, kyanite, and talc.

Other Applications. In addition to the minerals industry, flotation is finding a variety of new applications in other fields. The next largest application is for wastewater treatment to remove particulate, organic, and biological contaminants. Other applications include extraction of metallic values or removal of heavy metal compounds from hydrometallurgical streams by precipitate flotation, recovery of bitumen from tar sands, deinking of waste paper, recovery of solids from white water in paper making, recovery of glass sands from industrial wastes, removal of impurities from peas, removal of ergot from rye, separation of proteins from milk, and clarification of fruit juices. Ion flotation and foam fractionation are the slight modifications in the basic flotation process and are sometimes referred to as "adsorptive bubble separation." These methods are used for the extraction of soluble species.

GENERAL ASPECTS

Unit operation of flotation is based on two major steps: (1) *conditioning* and (2) *separation,* as is schematically depicted in Fig. 19-63. During the first step, the *slurry* or the *pulp,* consisting of particles to be separated, the particle size of which is already properly adjusted, is fed to the conditioning unit, to which the necessary flotation reagents are added. The main purpose of the conditioning step is to create physical-chemical conditions for achieving appropriate selectivity between particle species that are to be separated. The second step is then intended to generate and introduce air bubbles into the process vessel for contacting them with particulate species so as to affect their separation by flotation. Particles attached to the air bubbles are in most applications removed from the process vessel as froth. Accordingly,

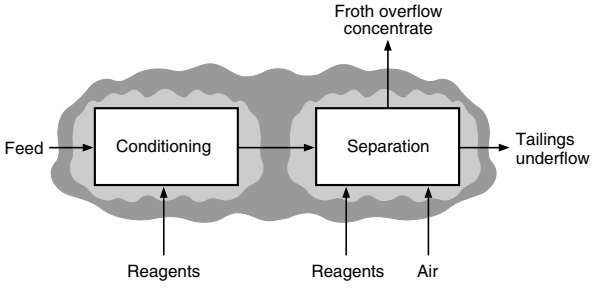


FIG. 19-63 Basic steps in a flotation system.

the unit operation of flotation is often referred to as *froth flotation.* The froth overflow stream is called a *concentrate* in the minerals industry, and the slurry underflow is termed *tailings.* Depending on the application, these two steps may be carried out in two distinctly different process units or in one combined unit.

Flotation Reagents. Three types of chemical reagents are used during the froth flotation process: collectors, frothers, and modifiers.

Collectors. These are surface-active agents that are added to the flotation pulp, where they adsorb selectively on the surface of the particles and render them hydrophobic. A convenient classification of the commonly used collectors is shown in Fig. 19-64. The nonionizing collectors (fuel oils and kerosene) are practically insoluble in water and cause the particles to become hydrophobic by covering them with a thin film. The ionizing collectors dissociate into ions in water and are made up of complex heteropolar molecules in that the molecule contains both a nonpolar hydrocarbon group with pronounced hydrophobic properties and a polar group with hydrophilic properties. The ionizing collectors adsorb either physically or chemically on the particle surface and can further be classified into anionic or cationic collectors depending on the nature of the nonpolar hydrocarbon group. Common examples of the ionizing collectors include fatty acids, long-chain sulfates, sulfonates and amines, xanthates, and dithiophosphates. Dosage requirements for collectors depend on the mechanisms by which they interact with the particle surface, but just enough is needed to form a monomolecular layer. As a rule, high dosages are required for nonionizing collectors and physisorbing ionizing collectors (in the order of 0.1 to 1 g of reagent per kg of solids) and low dosages for chemisorbing ionizing collectors (0.01 to 0.1 g of reagent per kg of solid). Addition of excess quantities of a collector is not desirable because it results in reducing the selectivity and increasing the cost.

Frothers. These are also surface-active agents added to the flotation pulp primarily to stabilize the air bubbles for effective particle-bubble attachment, carryover of particle-laden bubbles to the froth, and removal of the froth. The frother action is similar to the ionizing collectors except that they concentrate primarily at the air-liquid interface. Commonly used frothers are pine oil, cresylic acid, polypropylene glycol, short-chain alcohols, and 5- to 8-carbon aliphatic alcohols. Quantities of frothers required are usually 0.01 to 0.1 g per kg of solids.

Modifiers. Flotation modifiers include several classes of chemicals.

1. *Activators.* These are used to make a mineral surface amenable to collector coating. Copper ion is used, for example, to activate sphalerite (ZnS), rendering the sphalerite surface capable of absorbing a xanthate or dithiophosphate collector. Sodium sulfide is used to coat oxidized copper and lead minerals so that they can be floated by a sulfide mineral collector.
2. *pH regulators.* Regulators such as lime, caustic soda, soda ash, and sulfuric acid are used to control or adjust pH, a very critical factor in many flotation separations.
3. *Depressants.* Depressants assist in selectivity (sharpness of separation) or stop unwanted minerals from floating. Typical are sodium or calcium cyanide to depress pyrite (Fe_2S_2) while floating galena (PbS), sphalerite (ZnS), or copper sulfides; zinc sulfate to depress ZnS while floating PbS; sodium ferrocyanide to depress copper sulfides while floating molybdenite (MoS_2); lime to depress pyrite; sodium silicate to depress quartz; quebracho to depress calcite ($CaCO_3$) during fluorite (CaF_2) flotation; and lignin sulfonates and dextrins to depress graphite and talc during sulfide flotation.
4. *Dispersants and flocculants.* These are important for the control of slimes that sometimes interfere with the selectivity and increase reagent consumption. For example, soda ash, lime sodium silicate, and lignin sulfonates are used as dispersants, and starch and polyacrylamide are used as flocculants.

Quantities of modifying agents used vary widely, ranging from as little as 0.01 to 0.1 g/kg to as high as 1 to 2 g/kg of solids, depending upon the reagent and the metallurgical problem.

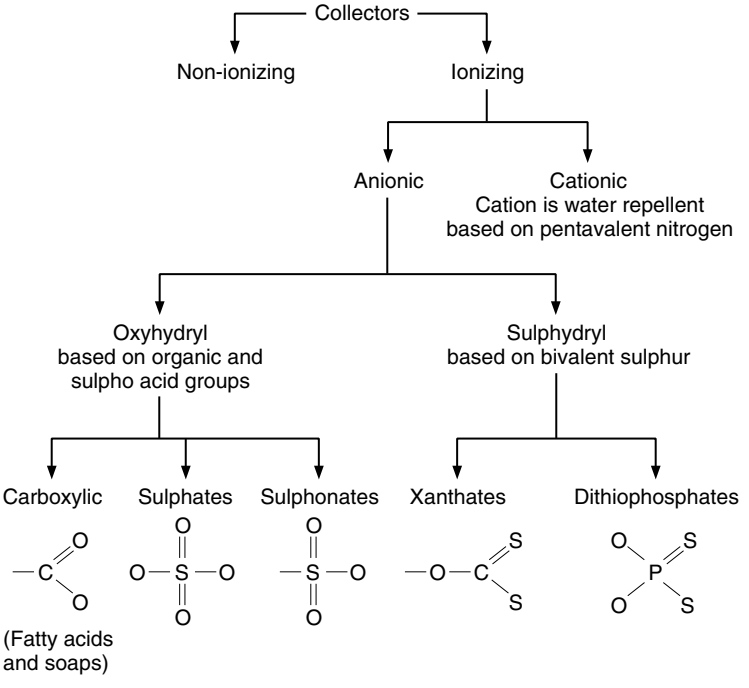


FIG. 19-64 Classification of collectors (after Glembotakii et al., 1972).

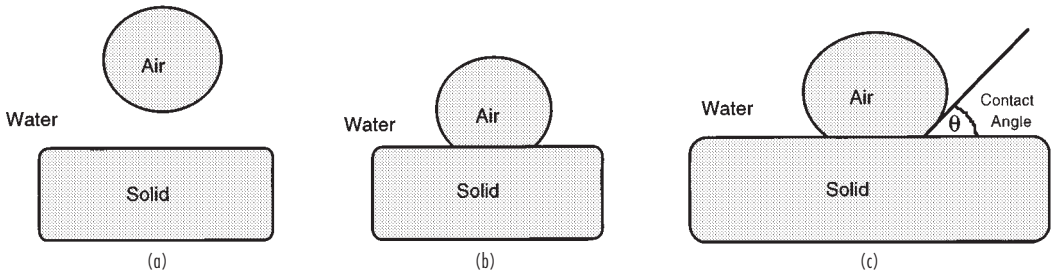


FIG. 19-65 Schematic representation of air bubble-water-solid particle system: (*a*) before, (*b*) after particle-bubble attachment, and (*c*) equilibrium force balance.

FUNDAMENTALS

Flotation is a physical process involving relative interaction of three phases: solid, water, and air. An understanding of the wettability of the solid surface, physical surface, and chemical phenomena by which the flotation reagents act and the mechanical factors that determine particle-bubble attachment and removal of particle-laden bubbles, is helpful in designing and operating flotation systems successfully.

Thermodynamics of Wetting. The fundamental objective of flotation is to contact solid particles suspended in water with air bubbles (Fig. 19-65*a*) and cause a stable bubble-particle attachment (Fig. 19-65*b*). It is seen that attachment of the particle to an air bubble destroys the solid-water and air-water interfaces and creates air-solid interface. The free energy change, on a unit area basis, is given by

$$\Delta G = \gamma_{AS} - (\gamma_{SW} + \gamma_{AW}) \tag{19-21}$$

where γ terms are the interfacial tensions of the air-solid (AS), solid-water (SW), and air-water (AW) interfaces, respectively. A force balance for the air-water-solid particle system (Fig. 19-65*c*) yields the familiar Young's Equation

$$\gamma_{AS} = \gamma_{SW} + \gamma_{AW} \cos \theta \tag{19-22}$$

where θ is the contact angle (measured through the water phase). It must be seen that the contact angle is an equilibrium measure of the interfacial energy of the air-water-solid system. Combining the above two equations, one obtains

$$\Delta G = \gamma_{AW}(\cos \theta - 1) \tag{19-23}$$

Thus, for any finite value of the contact angle, the free energy change becomes negative and particle-bubble attachment can take place. As mentioned above, polar solids have high surface energy and are wet by water. Therefore, the contact angle is zero. The wettability of solids can be controlled through adsorption of chemical reagents, which can change the interfacial tensions, so that the contact angle becomes finite and flotation can take place.

Physical-Chemical Phenomena. Several physical-chemical phenomena occur when chemical reagents are added to an air-water solid system due to the interaction of the reagents with the air-water, water-solid, and air-solid interfaces. This causes changes in the solution chemistry in which the particles are suspended. Some of the important phenomena that occur due to the addition of reagents include: solubility and dissociation of reagents in water, change of pH of the suspension, change of air-water surface tension, physical and chemical adsorption of the dissolved species on the solid surfaces due to hydrogen bond formation, electrostatic interactions, hydrophobic bonding, chemical bond formation, and fixation of reagent species in the solid lattice. All these phenomena in essence result in affecting the contact angle and flotation nature of solid particles and their attachment to air bubbles. A simplified pictorial representation of collector adsorption on particle surface, action of frother on the air bubble formation, and particle-bubble contact is shown in Fig. 19-66. An adequate understanding of the role played by the reagents and their proper choice to create the desired conditions is paramount to successful flotation.

Particle-Bubble Attachment. In the above, principles leading to creation of desired hydrophobicity/hydrophilicity of the particles has been discussed. The next step is to create conditions for particle-bubble contact, attachment, and their removal, which is simply described as a combination of three stochastic events with which are associated the probability of particle-bubble collision, probability of attachment, and probability of retention of attachment. The first term is controlled by the hydrodynamic conditions prevailing in the flotation unit. The second is determined by the surface forces. The third is dependent on the survival of the laden bubble by liquid turbulence and impacts by the other suspended particles. A detailed description of the hydrodynamic and other physical aspects of flotation is found in the monograph by Schulze (1984).

Process Variables. There are a number of variables that govern the flotation process. These include particle characteristics (size, shape, and chemical and mineralogical composition), chemical variables (type and amount of flotation reagents added), flotation machine variables (equipment size, internal geometry of the device, speed of operation, etc.) and operating variables (slurry feed rate and percent solids). A combined effect of all these variables can be represented by two independent variables—specific flotation rate (representing the rate of flotation of particles per unit time) and residence time of the pulp in the flotation device—and two dependent variables of grade (composition of the desired component) and recovery (ratio of the weight of the desired component in the froth product to that in the feed) of the froth product.

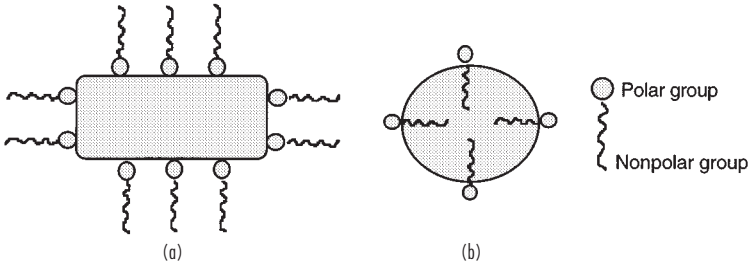


FIG. 19-66 Schematics of (*a*) collector adsorption at the particle-water interface and (*b*) action of the frother.

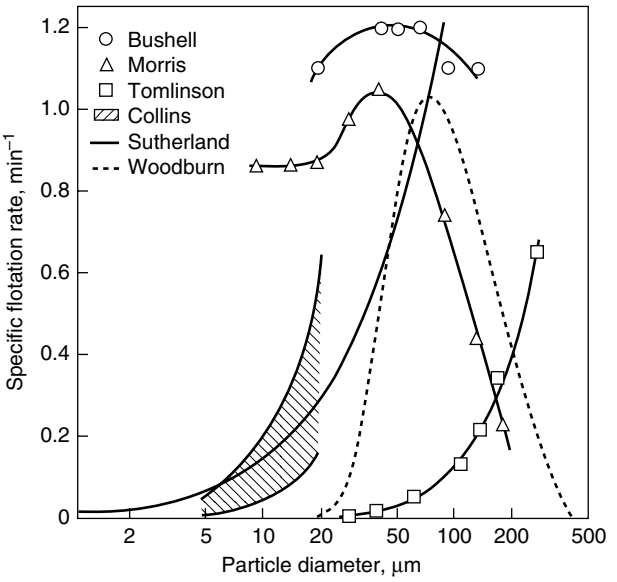


FIG. 19-67 Effect of particle diameter on specific flotation rate (Fuerstenau, 1980).

Several laboratory procedures are available to investigate the flotation response of any solid-solid system and in generating basic data for the selection and sizing of the flotation units and circuits. Also available are various process models for flotation with varying degrees of sophistication and representation. These process models can form a quantitative basis during all stages of engineering flotation systems. Finally, numerous types of flotation reagents and flotation equipment with different design details are currently available, and their proper choice has to be made depending on the kind of separation task one has on hand. Monographs listed in the general references provide a good starting point towards an understanding of these aspects.

Effect of Particle Size. Particle size is the most significant variable of flotation separation. The effect of particle size on the flotation rate is shown in Fig. 19-67. Particles in the size range of 20 to 60 μm have the highest flotation rate. Larger particles, being heavy, cannot be easily levitated and recovered, even though proper thermodynamic conditions might exist. In contrast, as particles become small, they become lighter and their surface-to-volume ratio becomes large. There are several factors that enter into making the flotation of small particles quite inefficient (Fig. 19-68).

EQUIPMENT

Various types of flotation machine designs can be classified into different categories based on the methods used for the generation and introduction of air bubbles into the equipment (Fig. 19-69). Each of the techniques of air bubble generation and particle-bubble contact along with the special features associated with different kinds of equipment has its own advantages and limitations. These must be considered carefully in selecting the equipment for a specific application. Individual manufacturers can provide basic help in selecting the equipment.

Electrolytic Flotation Units. Electrolytic or electroflotation is based on the generation of hydrogen and oxygen bubbles in a dilute aqueous solution by passing direct current between two electrodes. Choice of electrode materials include aluminum, platinized titanium, titanium coated with lead dioxide, and stainless steel of varying grades. Figure 19-70 illustrates the basic arrangement of an electrolytic flotation unit.

Electrical power to the electrodes is supplied at a low voltage potential of 5 to 10 volts. The power consumption is in the range of 0.5 to 0.7 kW/m^2 of flotation tank surface area depending on the conductiv-

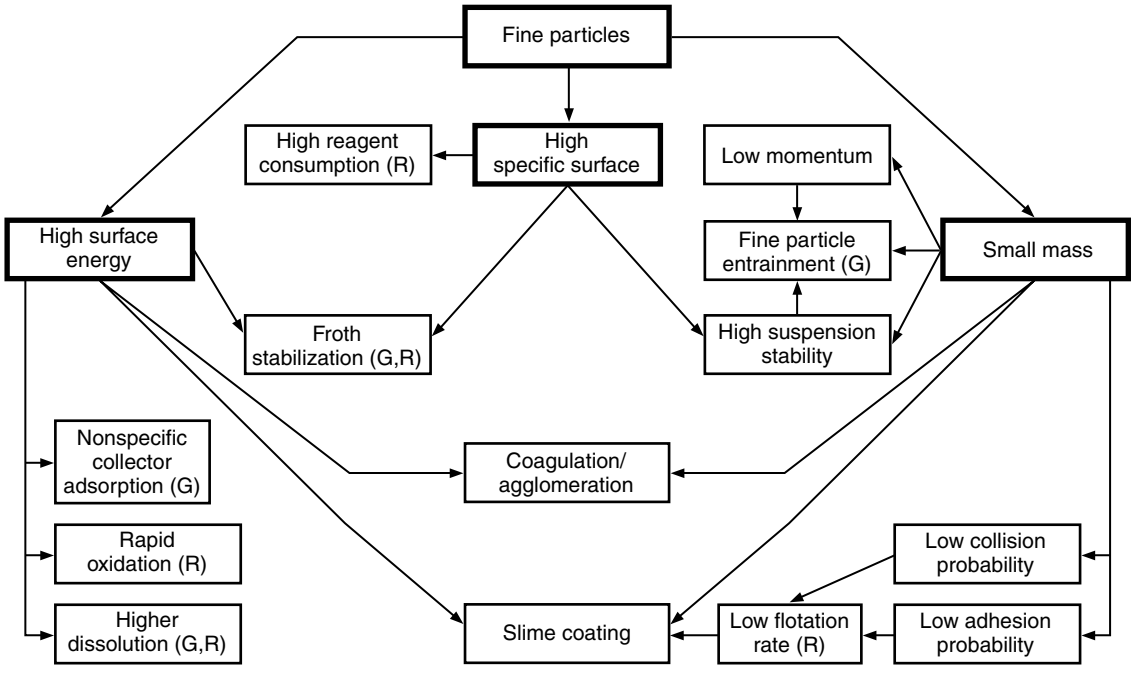


FIG. 19-68 The schematic diagram showing the relationship between the physical and chemical properties of fine particles and their behavior in flotation. (G) and (R) refer to whether the phenomena affects grade and/or recovery. The arrows indicate the various factors contributing to a particular phenomena observed in flotation of fine particles (Fuerstenau, 1980).

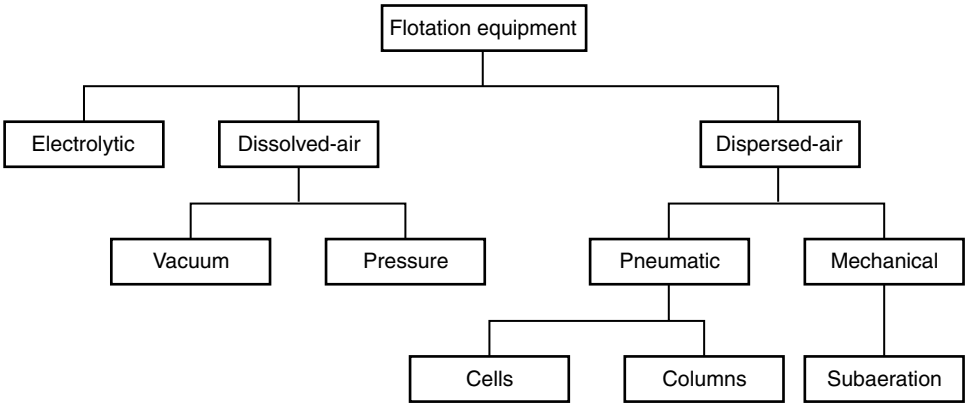


FIG. 19-69 Classification of flotation equipment based on the generation and introduction of air bubbles.

ity of the liquid and the distance between the electrodes. Such a unit produces approximately 50 to 1 of gas/h/m^2 of tank area. The main drawback of the electroflotation units is associated with the electrodes in terms of their fouling requiring mechanical cleaning devices and their consumption needing replacement at frequent intervals.

The bubble size in these cells tends to be the smallest (10 to 50 μm) as compared to the dissolved-air and dispersed-air flotation systems. Also, very little turbulence is created by the bubble formation. Accordingly, this method is attractive for the separation of small particles and fragile flocs. To date, electroflotation has been applied to effluent treatment and sludge thickening. However, because of their bubble generation capacity, these units are found to be economically attractive for small installations in the flow-rate range of 10 to 20 m^3/h. Electroflotation is not expected to be suitable for potable water treatment because of the possible heavy metal contamination that can arise due to the dissolution of the electrodes.

Dissolved-Air Flotation Units. Dissolved-air flotation entails saturating the process stream with air and generating air bubbles by releasing the pressure. Particle-bubble contact is achieved by the direct nucleation and growth of air bubbles on the particles, and very little mechanical agitation is employed. The dissolved-air precipitates in the form of fine bubbles in the size range of 20 to 100 μm. This method of air bubble generation does not require the addition of frother-type chemical reagents and often limits the total quantity of aeration possible. As such, dissolve-air flotation systems are used to treat process streams with low solids concentration (0.01 to 2 percent by volume). Vacuum flotation and pressure flotation are the two main types of dissolved-air flotation processes, with the latter being most widely used.

In vacuum flotation, the process stream is saturated with air at atmospheric pressure and introduced to the flotation tank on which a vacuum is applied, giving rise to the generation of the air bubbles. The process can be run only as a batch process and requires sophisticated equipment to produce and maintain the vacuum. By and large, the amount of air released during flotation is limited by the vacuum achievable.

In contrast to vacuum flotation, dissolved-air flotation units can be operated on a continuous basis by the application of pressure. This consists of pressurizing and aerating the process stream and introducing it into the flotation vessel that is maintained at the atmospheric pressure. The reduction of pressure results in the formation of fine air bubbles and the collection of fine particulates to be floated and removed as sludge.

Pressurization could be carried out on the entire feed stream (full-flow pressure flotation) or a fraction of the feed stream while the remainder is introduced directly without aeration into the flotation tank (split-flow pressure flotation). The split-flow system offers a cost saving over the full-flow units, since only a portion of the influent needs to be pressurized. In both cases, however, if the solid particles in the feed stream are flocculated before introducing to the flotation tank, the high shear during pressurization, aeration, and pressure release can destroy the flocs. Also, if the particle loading in the feed stream is high, both systems are susceptible to blockage of the air release devices. To minimize these problems, recycle-flow pressure flotation is often practiced (Fig. 19-71). In this process, the feed stream, flocculated or otherwise, is introduced directly into the process vessel, and part of the clarified effluent is pressurized, aerated, and recycled to the flotation tank in which it is mixed with the flocculated feed. The air bubbles are released as they attach to the flocs and float to the tank surface. The recycle-flow devices are found to offer the highest unit capacities.

Figure 19-72 illustrates a dissolved-air flotation plant flowsheet for water treatment. The flowsheet shows that the incoming raw water is

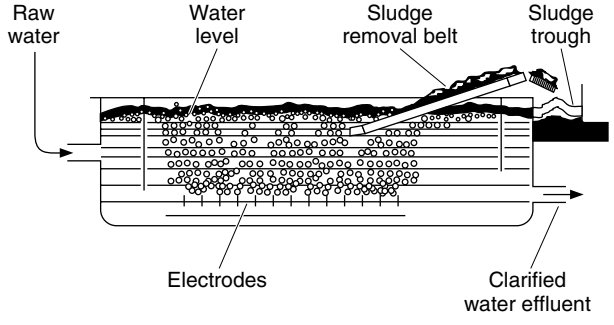


FIG. 19-70 Schematic diagram of an electrolytic flotation plant.

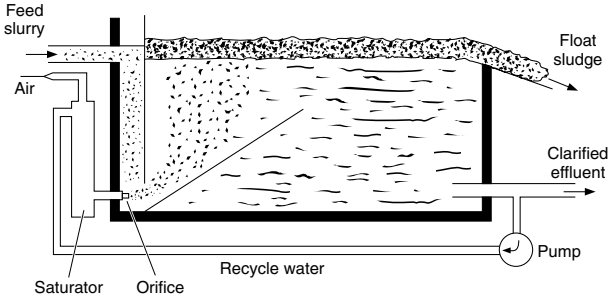


FIG. 19-71 Schematic diagram of a dissolved air flotation plant.

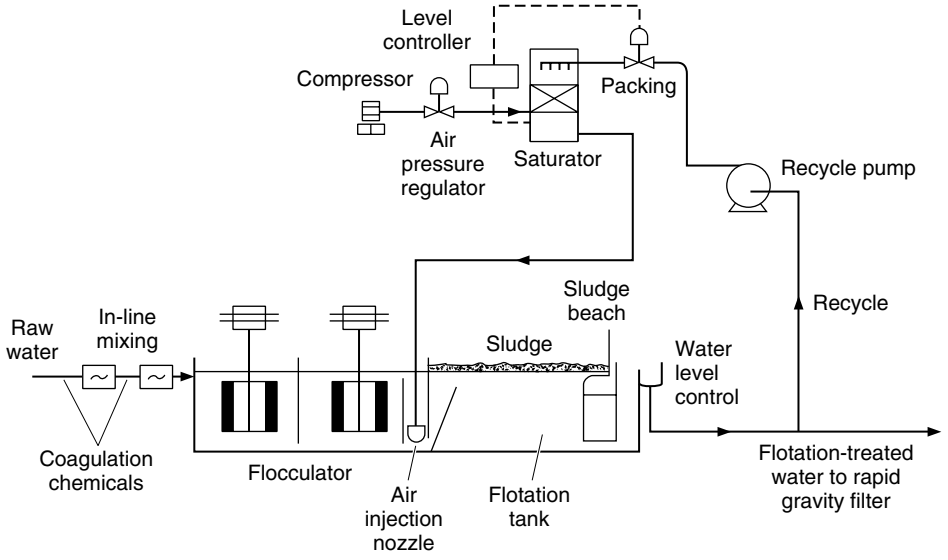


FIG. 19-72 Schematic diagram of a recycle dissolved-air flotation plant for water treatment.

conditioned with the addition of coagulation chemicals in a flocculator. This device pressurizes and aerates part of the treated water and recycles it to the flotation unit.

The dissolved-air flotation process is most commonly used for sewage and potable water treatment. It is also gaining popularity for the treatment of slaughterhouse, poultry processing, seafood processing, soap, and food processing wastes (Zoubulis et. al., 1991).

Dispersed-Air Flotation Units. Dispersed-air flotation involves the generation of air bubbles, either pneumatically or by mechanical means. In both cases, relatively large air bubbles (at least 1 mm in size) are generated. In order to control the size and stability of air bubbles, frothers are added to the flotation devices. These devices represent the workhorses of the minerals industry in beneficiating metallic and nonmetallic ore bodies and cleaning of high-ash and high-sulfur coals in which feed streams contain relatively high percent solids (5 to 50 percent by volume), and high throughputs are maintained (in excess of 4000 t/h). Handling of large quantities of solids in these flotation devices requires such special design considerations as maintaining the solids in suspension, promoting particle-bubble collisions leading to attachment, providing a quiescent pulp region below the froth to minimize pulp entrainment, and finally providing sufficient froth depth to permit washing and drainage of hydrophilic solids entering the froth region.

Mechanical flotation machines are most commonly used in the mineral industry, while pneumatic column-type units are gaining popularity in recent years. Surveys by Harris (1976), Young (1982), Barbery (1982), and Mavros (1991) provide a detailed overview of the process-engineering aspects of mineral flotation devices in particular and systems in general.

Mechanical Cells. Figure 19-73 presents a schematic representation of a typical mechanical device commonly known as a *flotation cell.* It is characterized by a cubic or cylindrical shape, equipped with an impeller surrounded by baffles with provisions for introduction of the feed slurry and removal of froth overflow and tailings underflow. The machines receive the supply of air through a concentric pipe surrounding the impeller shaft, either by self-aeration due to the pressure drop created by the rotating impeller or by air injection by means of an external blower. In a typical installation, a number of flotation cells are connected in series such that each cell outputs froth into a launder and the underflow from one cell goes to the next one. The cell design may be such that the flow of slurry from one cell to another can either be "restricted" by weirs or unrestricted.

The mechanical cells that are most widely used today in sulfide, coal, and nonmetallic flotation operations in the western hemisphere are made by Fagergren (by WEMCO Division of Envirotech Corporation), D-R Denver (by Denver Equipment Corporation of Sala International), Agitair (supplied by Galligher Ash Company), and Outokumpy (by Outokumpu Oy).

These machines provide mechanical agitation and aeration by means of a rotation impeller on an upright shaft. In addition, the Agitair and Denver cells also utilize air from a blower to help aerate the pulp.

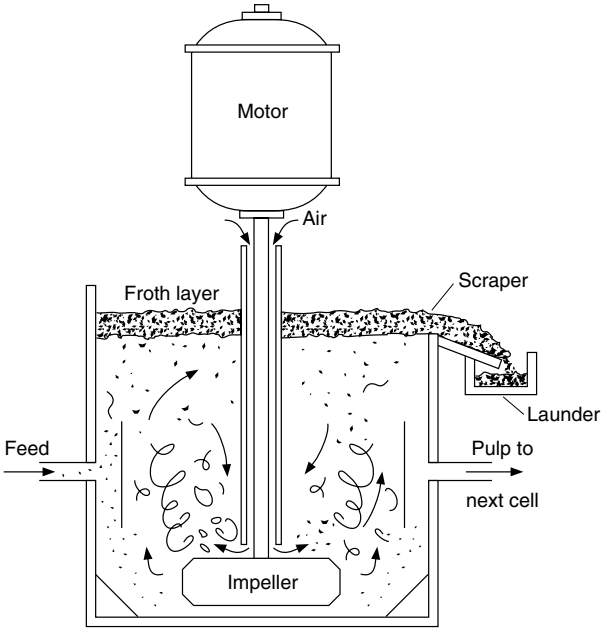


FIG. 19-73 Schematic of a mechanical flotation cell.

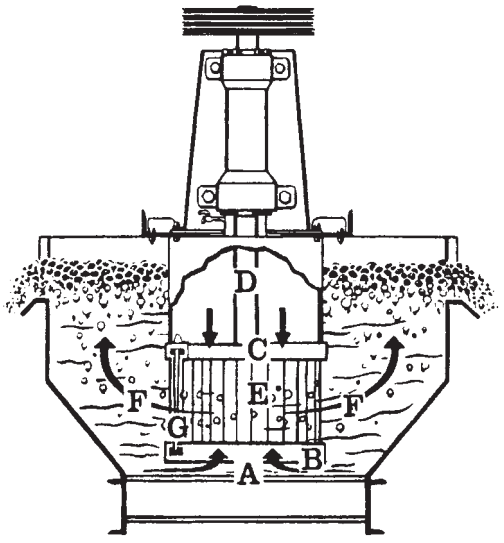


FIG. 19-74 Fagergren flotation machine.

In the Fagergren machine (Fig. 19-74), pulp is drawn upward into the rotor *A* by the rotor's lower portion *B*. Simultaneously the rotor's upper end *C* draws air down the standpipe *D* for thorough mixing with the pulp inside the rotor *E*. The aerated pulp is then expelled by a strong centrifugal force *F*. The shearing action of the stator *G*, a stationary cage fitting closely around the rotor, breaks the air into minute bubbles. This action uniformly distributes a large volume of air in the form of minute bubbles in all parts of the cell.

In the D-R Denver machine (Fig. 19-75), the pulp enters the top of the recirculation well *A*, while the low-pressure air enters through the air passage *B*. Pulp and air are intimately mixed and thrown outward by the rotating impeller *C* through the stationary diffuser *D*. The collector-coated mineral particles adhere to be removed in the froth product.

In the Agitair flotation machine (Fig. 19-76), the impeller is a flat rubber-covered disk with steel fingers extending downward from the periphery. A rubber-covered stabilizer eliminates dead spots in the agitation zone and improves bubble-ore contact. The degree of aeration is controlled by regulating air volume on each cell with an individual air valve. Air is supplied at 10×10^3 Pa (1.5 lbf/in^2).

Modern mineral-processing plants are being designed with capacities on the order of 500 to 1000 kg/s (2000 to 4000 tons/h). The unit capacities of flotation machines now being manufactured are 10 times greater than those in common use 15 to 20 years ago (Fig. 19-76). Examples of large flotation cells that are currently available on the market include Denver Equipment (36.1 m^3), Agitair (42.5 m^3), and Wemco (85 m^3). Larger-scale flotation machines offer advantages of lower installed cost, lower operating cost, and lower floor-space requirements. However, it should be noted that large flotation cells do not permit a reduction in the number of cells in a series. The use of large flotation cells does enable a fewer number of parallel rows and thereby permits a reduction in pumps, piping, and other auxiliaries.

Flotation Columns. Flotation columns belong to the class of pneumatic devices in that air-bubble generation is accomplished by a gas-sparging system and no mechanical agitation is employed. Columns are built of long tubes of either circular or square cross sections that are commonly fitted with internal baffling. They are usually 10 or even 15 m high with a cross sectional area of 5 to 10 m^2. Figure 19-78 presents a schematic of a typical flotation column unit. Inputs to the column include preconditioned slurry feed and air and washwater spray, which are introduced at about two-thirds of the height from the bottom, in the bottom region, and at the top of the column, respectively. The outputs are froth overflow, consisting of hydrophobic particles from the top, and underflow from the bottom of the column, carrying the nonfloatable hydrophilic particles. Flotation columns

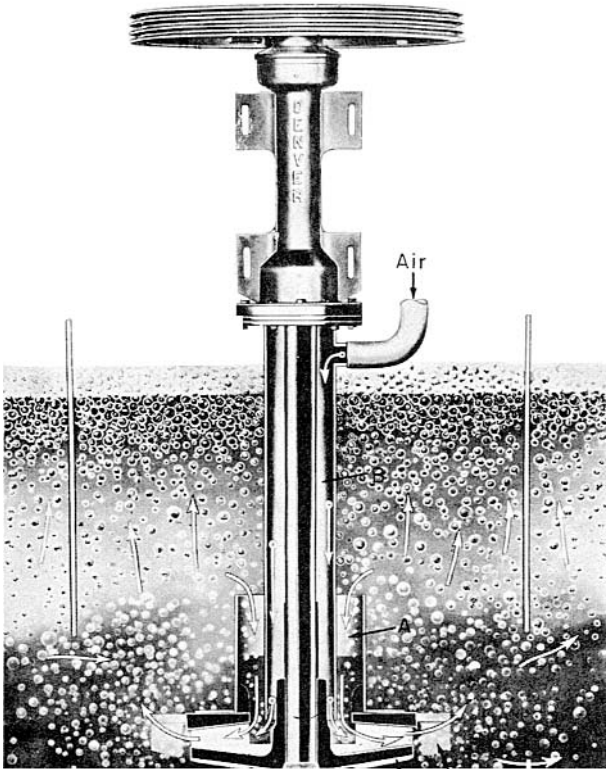


FIG. 19-75 D-R Denver flotation machine.

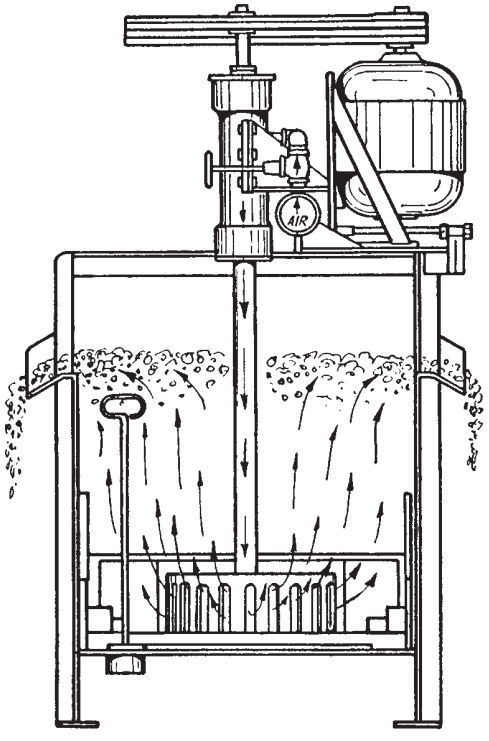


FIG. 19-76 Agitair flotation machine.

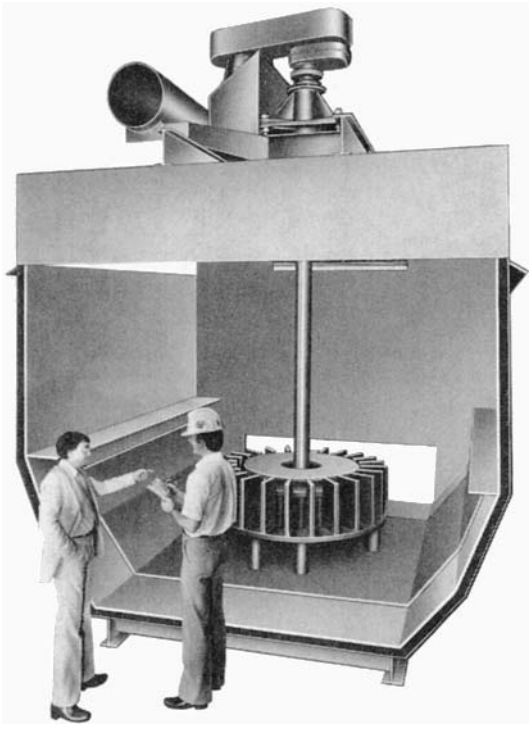


FIG. 19-77 Large flotation cell No. 165 AX 1500 Agitair, 42.5 m^3 (1500 ft^3). (*Courtesy of Caligher Ash Company.*)

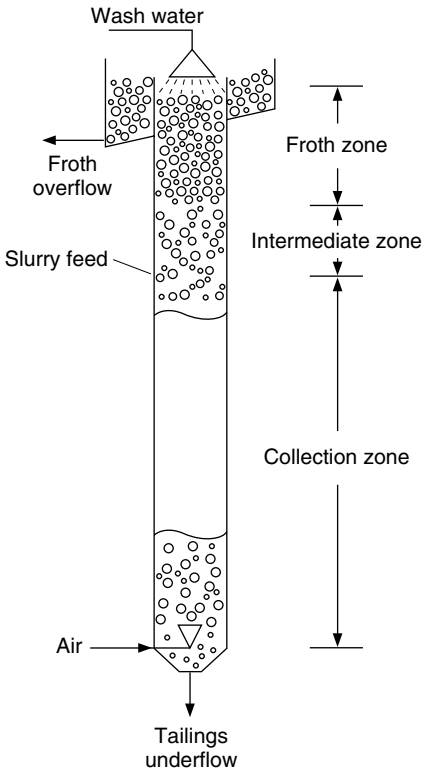


FIG. 19-78 Schematic of a flotation column.

make use of the countercurrent flow principle in that the swarm of air bubbles rises through the downward-flowing slurry during which time transfer of hydrophobic particles occurs between the slurry and bubble phases. The particle transfer process occurs in three distinct zones known as collection, intermediate, and froth zones. Properly designed baffles reduce short circuiting and promote better bubble-particle contact. Recovery of hydrophobic particles by the air bubbles takes place in the collection zone. Underflow removal rate and washwater addition rate are regulated such that there exists downward flow of slurry throughout the height of the column, thus ensuring that there is no bypass of the feed slurry in the upward direction. Further, the downward pattern of the flow of liquid helps in minimizing the entrainment of hydrophilic particles with the uprising air bubbles in the collection zone and in stripping the hydrophilic particles attached to the air bubbles in all three regions. All in all, the performance of the columns in terms of the recovery of hydrophobic particles and the grade of the froth concentrate is determined primarily by the slurry feed rate, air flow rate, and the surface area of the air bubbles.

Because of their inherently simple design, it is fairly common for flotation columns to be constructed in-house except for using the patented air-sparging systems. Several sparger designs are available that include simple porous plugs made from glass, stainless steel, and rubber, or more sophisticated venturi or in-line mixer configurations (Finch and Dobby, 1990). Some of the advantages claimed with flotation columns include improved separation performance, particularly for fine materials; low capital and operating costs; low plant floorspace requirements; and easy adaptability to automatic control. Flotation columns are being used in iron ore, copper, lead, zinc, and coal flotation applications and are expected to become even more popular because of their simplicity in construction and flexibility of operation.

Several modifications to the basic column design have become available over the years. Figure 19-79 shows three such designs. The first design variation is a packed column (Fig. 19-79*a*), which represents a minor variation to the basic column design in that it provides for corrugated plate-type packing. The packing feature enables uniform bubble size throughout the height, intimate particle-bubble contact, increased residence time of the slurry and bubble phases in the column, and a deeper froth zone (Yang, 1988). The Jameson cell (Fig. 19-79*b*), by contrast, is a combination column-cell design. It includes a vertical downcomer column in which the air and pulp are dispersed into a dense foam of fine bubbles creating a favorable environment for particle-bubble contact. The bubbly mixture is then discharged into a cell, which allows the separation of particle-laden bubbles from the pulp (Clayton et. al., 1991). Air-sparged hydrocyclone (Figure 19-79*c*) is a distinctly different design consisting of two concentric tubes with a conventional cyclone header at the top, providing for a tangential entry of the feed. As the feed slurry swirls down the inner porous tube through which air is sparged, collision between centrifuged particles and air bubbles takes place, leading to the recovery of hydrophobic particles. The bubble-hydrophobic particle aggregates are transported into the overflow stream as froth, while the nonfloating particles are removed with the underflow (Miller et al., 1988). Each of these and other design variations to the basic pneumatic flotation column concept is found to offer process improvements to specific applications.

Monographs by Sastry (1988), Finch and Dobby (1990), and Rubinstein (1994) provide an overview of the design and operational aspects of flotation columns.

FLOTATION PLANT OPERATION

Ores must be ground to a point of complete or nearly complete liberation. Even though this might possibly be accomplished by coarse crushing, grinding to finer than 10 mesh in all cases and finer than 48 mesh in most cases is necessary prior to flotation. Grinding is done in closed circuit with classifiers.

In many instances, superior flotation results are obtained by conditioning the ore with the reagents before the flotation step. Oily-type collectors are sometimes added to the grinding circuit to ensure dis-

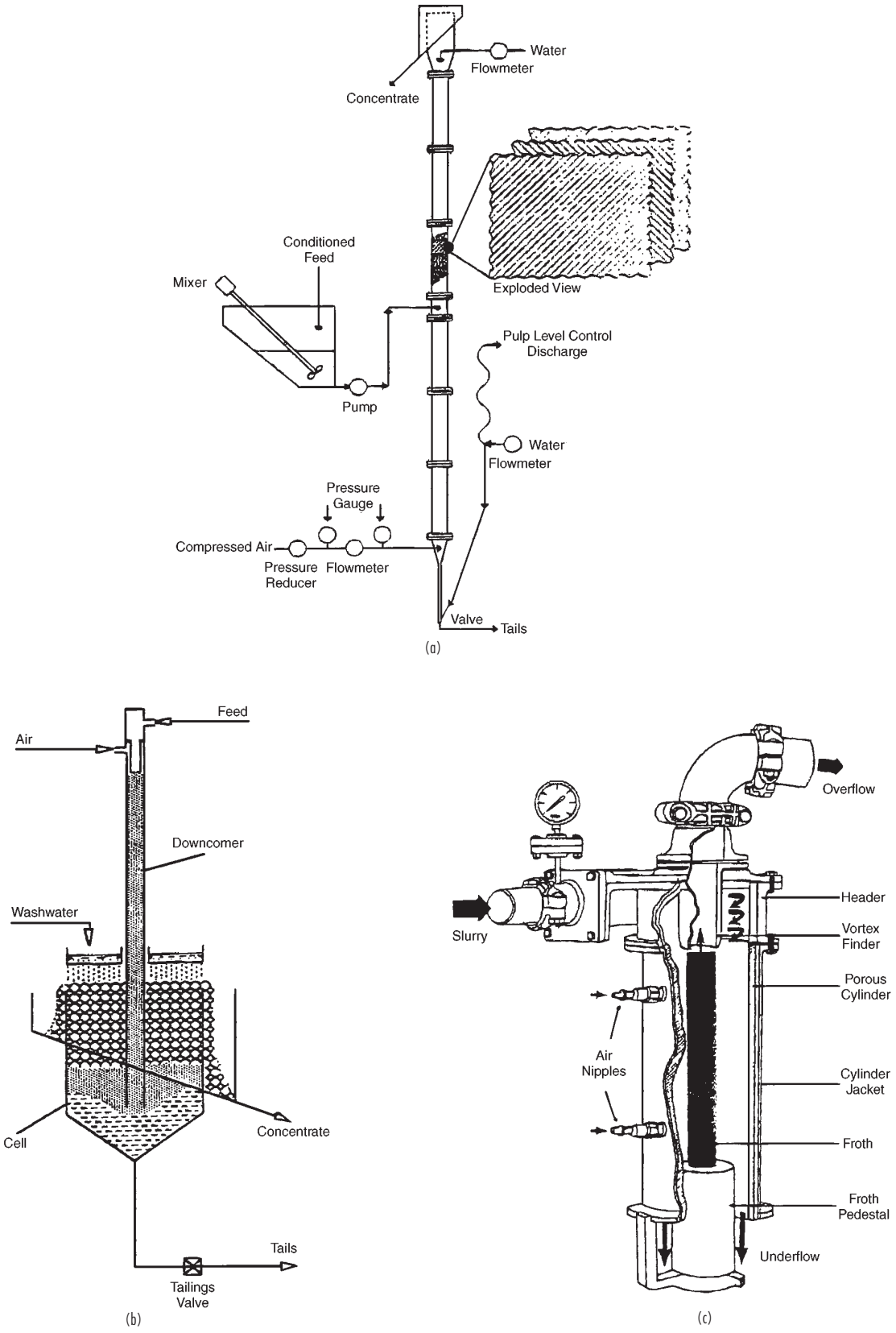


FIG. 19-79 Variations in the basic column design: (*a*) packed column, (*b*) Jameson cell, and (*c*) air-sparged hydrocyclone.

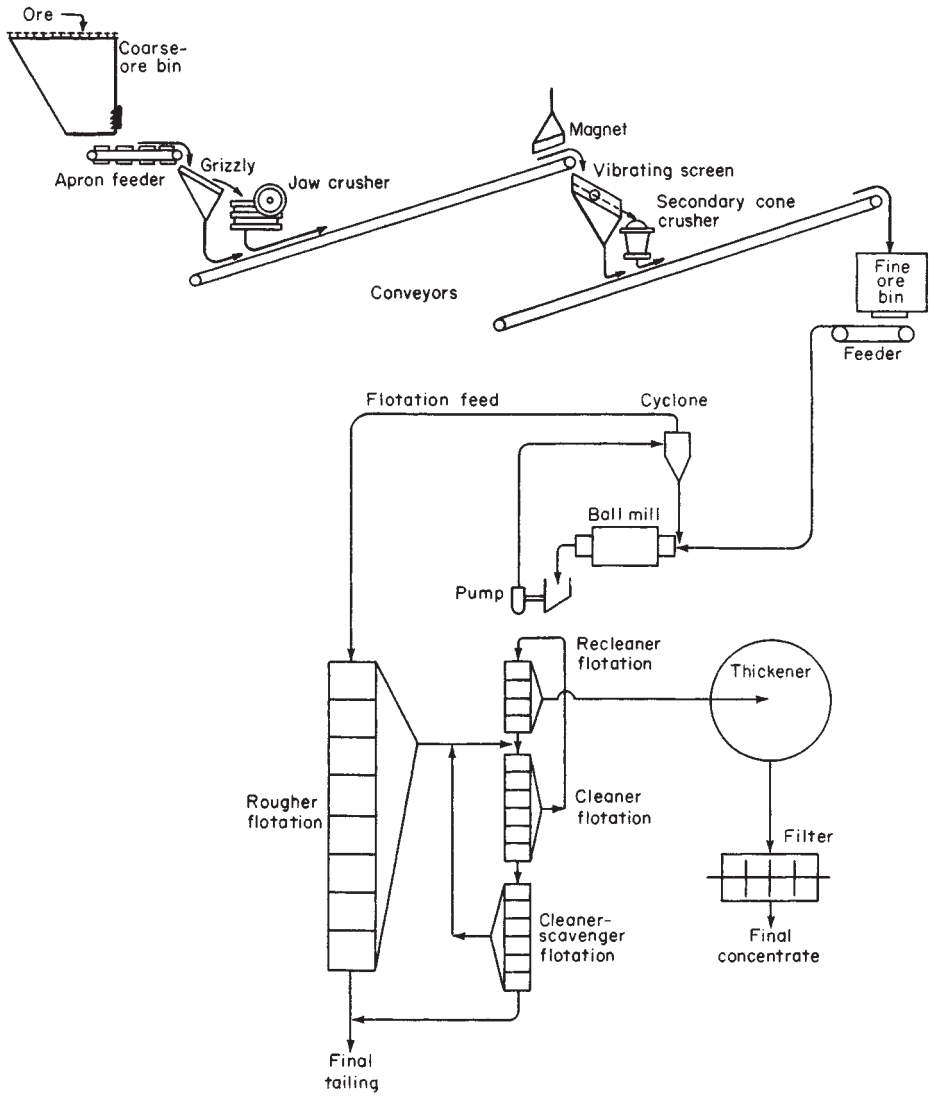


FIG. 19-80 Flowsheet of a typical flotation plant.

persion. For proper selectivity, a definite contact time is sometimes required between reagent and ore, and this is usually secured by mixing the reagent and the ore pulp in a conditioner consisting of a cylindrical tank with a vertical impeller.

Flotation machines are built in multiple units, and the flow of the pulp through the various units is adjusted for the best results. Common practice is to feed the pulp to several cells known as *roughers*, which produce a barren tailing and low-grade concentrate. The concentrate is treated, sometimes after regrinding, in *cleaner* cells and *recleaner* cells for final concentration. The tailing from the cleaner and recleaner cells are recirculated back through the system or concentrated separately in additional cells. Regrinding of these middlings is necessary in many ores.

Important auxiliary equipment in a flotation plant includes feeder and controls, sampling and weighing devices, slurry pumps, filter and thickeners for dewatering solids, reagent storage and makeup equipment, and analytical devices for process control.

Figure 19-80 is a flowsheet of a typical flotation plant.

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Size Reduction and Size Enlargement

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Nomenclature and Units for Size Enlargement and Practice

Symbol	Definition	SI units	U.S. customary units	Symbol	Definition	SI units	U.S. customary units
A	Parameter in Eq. (20-47)			k	Coalescence rate constant	1/s	1/s
A	Apparent area of indentor contact	cm^2	in^2	K	Agglomerate deformability		
A	Attrition rate	cm^3/s	in^3/s	K_c	Fracture toughness	$MPa{\cdot}m^{1/2}$	$MPa{\cdot}m^{1/2}$
A_t	Spouted-bed inlet orifice area	cm^2	in^2	l	Wear displacement of indentor	cm	in
B	Nucleation rate	cm^3/s	in^3/s	L	Roll loading	dyn	lbf
B_f	Fragmentation rate	g/s	lb/s	$(\Delta L/L)_c$	Critical agglomerate deformation strain		
B_f	Wear rate	g/s	lb/s	N_t	Granules per unit volume	$1/cm^3$	$1/ft^3$
c	Crack length	cm	in	n	Feed droplet size	cm	in
δ_c	Effective increase in crack length due to process zone	cm	in	$n(v,t)$	Number frequency size distribution by size volume	$1/cm^6$	$1/ft^6$
c	Unloaded shear strength of powder	kg/cm^2	psf	N_c	Critical drum or disc speed	rev/s	rev/s
d	Harmonic average granule diameter	cm	in	P	Applied load	dyn	lbf
d	Primary particle diameter	cm	in	P	Pressure in powder	kg/cm^2	psf
d	Impeller diameter	cm	in	Q	Maximum compressive force	kg/cm^2	psf
d	Roll press pocket depth	cm	in	Q	Granulator flow rate	cm^3/s	ft^3/s
d_i	Indentor diameter	cm	in	r_p	Process zone radius	cm	in
d_p	Average feed particle size	cm	in	R	Capillary radius	cm	in
D	Die diameter	cm	in	S	Volumetric spray rate	cm^3/s	ft^3/s
D	Disc or drum diameter	cm	in	St	Stokes number, Eq. (20-48)		
D	Roll diameter	cm	in	St*	Critical Stokes number representing energy required for rebound		
D_c	Critical limit of granule size	cm	in				
e_r	Coefficient of restitution			St_0	Stokes number based on initial nuclei diameter		
E	Strain energy stored in particle	J	J				
E^*	Reduced elastic modulus	kg/cm^2	psf	t	Time	s	s
f_c	Unconfined yield stress of powder	kg/cm^2	psf	u,v	Granule volumes	cm^3	in^3
g	Acceleration due to gravity	cm/s2	ft/s2	u_0	Relative granule collisional velocity	cm/s	in/s
G_c	Critical strain energy release rate	J/m^2	J/m^2	U	Fluidization gas velocity	cm/s	ft/s
F	Indentation force	dyn	lbf	U_{mf}	Minimum fluidization gas velocity	cm/s	ft/s
F	Roll separating force	dyn	lbf	U_i	Spouted-bed inlet gas velocity	cm/s	ft/s
G	Layering rate	cm^3/s	in^3/s	V	Volumetric wear rate	cm^3/s	in^3/s
h	Height of liquid capillary rise	cm	in	V_R	Mixer swept volume ratio of impeller	cm^3/s	ft^3/s
h	Roll press gap distance	cm	in	V	Volume of granulator	cm^3	ft^3
h	Binder liquid layer thickness	cm	in	w	Weight fraction liquid		
h_b	Fluid-bed height	cm	in	w	Granule volume	cm^3	in^3
h_a	Height of surface asperities	cm	in	w^*	Critical average granule volume	cm^3	in^3
h_e	Maximum height of liquid capillary rise	cm	in	W	Roll width	cm	in
H	Individual bond strength	dyn	lbf	x	Granule or particle size	cm	in
H	Hardness of agglomerate or compact	kg/cm^2	psf	y	Liquid loading		
				Y	Calibration factor		
				Greek symbols			
$\beta(u, v)$	Coalescence rate constant for collisions between granules of volumes u and v	1/sec	1/sec	$\Delta\rho$	Relative fluid density with respect to displaced gas or liquid	gm/cm^3	
				ρ	Apparent agglomerate or granule density	gm/cm^3	lb/ft^3
ε	Porosity of packed powder			ρ_a	Apparent agglomerate or granule density	gm/cm^3	lb/ft^3
ε_b	Interagglomerate bed voidage			ρ_b	Bulk density	gm/cm^3	lb/ft^3
ε_g	Intraagglomerate granule porosity			ρ_g	Apparent agglomerate or granule density	gm/cm^3	lb/ft^3
κ	Compressibility of powder			ρ_l	Liquid density	gm/cm^3	lb/ft^3
ϕ	Disc angle to horizontal	deg	deg	ρ_s	True skeletal solids density	gm/cm^3	lb/ft^3
ϕ	Internal angle of friction	deg	deg	σ_0	Applied axial stress	kg/cm^2	psf
ϕ_e	Effective angle of friction	deg	deg	σ_z	Resulting axial stress in powder	kg/cm^2	psf
ϕ_w	Wall angle of friction	deg	deg	σ	Powder normal stress during shear	kg/cm^2	psf
ϕ_w	Roll friction angle	deg	deg	σ_c	Powder compaction normal stress	kg/cm^2	psf
$\varphi(\eta)$	Relative size distribution			σ_f	Fracture stress under three-point bend loading	kg/cm^2	psf
γ^{lv}	Liquid-vapor interfacial energy	dyn/cm	dyn/cm	σ_T	Granule tensile strength	kg/cm^2	psf
γ^{sl}	Solid-liquid interfacial energy	dyn/cm	dyn/cm	σ_y	Granule yield strength	kg/cm^2	psf
γ^{sv}	Solid-vapor interfacial energy	dyn/cm	dyn/cm	τ	Powder shear stress	kg/cm^2	psf
μ	Binder or fluid viscosity	poise		θ	Contact angle	°	°
μ	Coefficient of internal friction			ς	Parameter in Eq. (20-47)		
ω	Impeller rotational speed	rad/s	rad/s	η	Parameter in Eq. (20-47)		

Nomenclature and Units

Symbol	Definition	SI units	U.S. customary units	Symbol	Definition	SI units	U.S. customary units
A	Coefficient in double Schumann equation			q_f	Fine-fractiom mass flow rate	g/s	lb/s
				q_o	Feed mass flow rate	g/s	lb/s
a	Constant			q_p	Mass flow rate of classifier product	g/s	lb/s
$a_{k,k}$	Coefficient in mill equations			q_R	Mass flow rate of classifier tailings	g/s	lb/s
$a_{k,n}$	Coefficient in mill equations			q_R	Recycle mass flow rate to a mill	g/s	lb/s
$\mathbf{B}$	Matrix of breakage function			R	Recycle		
$\Delta B_{k,u}$	Breakage function			R	Reid solution		
b	Constant			r	Dimensionless parameter in size-distribution equations		
C	Constant						
C_s	Impact-crushing resistance	kWh/cm	(ft·lb)/in	S	Rate function	S^{-1}	S^{-1}
D	Diffusivity	m^2/s	ft^2/s	$\overline{S}$	Corrected rate function	S^{-1}	S^{-1}
D	Mill diameter	m	ft	$\mathbf{S'}$	Matrix of rate function	Mg/kWh	ton/(hp·h)
D_b	Ball or rod diameter	cm	in	$S_G(X)$	Grindability function	S^{-1}	S^{-1}
D_{mill}	Diameter of mill	m	ft	S_u	Grinding-rate function		
d	Differential			s	Parameter in size-distribution equations		
d	Distance between rolls of crusher	cm	in				
E	Work done in size reduction	kWh	hp·h	s	Peripheral speed of rolls	cm/min	in/min
E	Energy input to mill	kW	hp	t	Time	s	s
E_i	Bond work index	kWh/Mg	(hp·h)/ton	u	Settling velocity of particles	cm/s	ft/s
E_i	Work index of mill feed			$\mathbf{W}$	Vector of differential size distribution of a stream		
E_2	Net power input to laboratory mill	kW	hp				
erf	Normal probability function			w_k	Weight fraction retained on each screen		
F	As subscript, referring to feed stream						
F	Bonding force	kg/kg	lb/lb	w_u	Weight fraction of upper-size particles		
g	Acceleration due to gravity	cm/s^2	ft/s^2	w_t	Material holdup in mill	g	lb
$\mathbf{I}$	Unit matrix in mill equations			X	Particle size or sieve size	cm	in
i	Tensile strength of agglomerates	kg/cm^2	lb/in^2	X'	Parameter in size-distribution equations	cm	in
K	Constant						
k	Parameter in size-distribution equations	cm	in	ΔX_i	Particle-size interval	cm	in
k	As subscript, referring to size of particles in mill and classifier parameters			X_i	Midpoint of particle-size interval, ΔX_i	cm	in
				X_0	Constant, for classifier design		
				X_f	Feed-particle size	cm	in
L	As subscript, referring to discharge from a mill or classifier			X_m	Mean size of increment in size-distribution equations	cm	in
L	Length of rolls	cm	in	X_p	Product-particle size	cm	in
L	Inside length of tumbling mill	m	ft	X_p	Size of coarser feed to mill	cm	in
$\mathbf{M}$	Mill matrix in mill equations			X_{25}	Particle size corresponding to 25 percent classifier-selectivity value	cm	in
m	Dimensionless parameter in size-distribution equations			X_{50}	Particle size corresponding to 50 percent classifier-selectivity value	cm	in
N	Mean-coordination number						
N_c	Critical speed of mill	r/min	r/min	X_{75}	Particle size corresponding to 75 percent classifier-selectivity value	cm	in
ΔN	Incremental number of particles in size-distribution equation			ΔX_k	Difference between opening of successive screens	cm	in
n	Dimensionless parameter in size-distribution equations			x	Weight fraction of liquid		
n	Constant, general			Y	Cumulative fraction by weight undersize in size-distribution equations		
n_r	Percent critical speed of mill						
O	As subscript, referring to inlet stream			Y	Cumulative fraction by weight undersize or oversize in classifier equations		
P	As subscript, referring to product stream			ΔY	Fraction of particles between two sieve sizes		
P_k	Fraction of particles coarser than a given sieve opening			ΔY	Incremental weight of particles in size-distribution equations	g	lb
p	Number of short-time intervals in mill equations			ΔY_{ci}	Cumulative size-distribution intervals of coarse fractions	cm	in
Q	Capacity of roll crusher	cm^3/min	ft^3/min				
q	Total mass throughput of a mill	g/s	lb/s	ΔY_{fi}	Cumulative size-distribution intervals of fine fractions	cm	in
q_c	Coarse-fraction mass flow rate	g/s	lb/s				
q_F	Mass flow rate of fresh material to mill	g/s	lb/s	$\mathbf{Z}$	Matrix of exponentials		

Greek symbols

β	Sharpness index of a classifier			ρ_ℓ	Density of liquid	g/cm^3	lb/in^3
δ	Angle of contact	rad	0	ρ_s	Density of solid	g/cm^3	lb/in^3
ε	Volume fraction of void space			Σ	Summation		
Z	Residence time in the mill	s	s	σ	Standard deviation		
η_s	Size-selectivity parameter			σ	Surface tension	N/cm	dyn/cm
μ	Viscosity of fluid	$(N·S)/m^2$	P	υ	Volumetric abundance ratio of gangue to mineral		
ρ_f	Density of fluid	g/cm^3	lb/in^3				

PARTICLE-SIZE ANALYSIS

General References: Allen, *Particle Size Measurement,* Chapman and Hall, 4th ed. 1990. Barth and Sun, *Particle Size Analysis Review,* Anal. Chem., 57, 151R, 1985. Miller and Lines, *Critical Reviews in Analytical Chemistry,* **20**(2), 75–116, 1988. Herdan, *Small Particle Statistics,* Butterworths, London. Orr and DalleValle, *Fine Particle Measurement,* Macmillan, New York, 2d ed., 1960. Kaye, *Direct Characterization of Fine Particles,* Wiley, New York, 1981. Van de Hulst, *Light Scattering by Small Particles,* Wiley, New York, 1957.

PARTICLE-SIZE DISTRIBUTION

Specification for Particulates Feed, recycle, and product from size reduction operations are defined in terms of the sizes involved. It is also important to have an understanding of the degree of aggregation or agglomeration that exists in the measured distribution.

The fullest description of a powder is given by its **particle-size distribution.** This can be presented in tabular or graphical form. The simplest presentation is in linear form with equal size intervals (Table 20-1). The significance of the distribution is more easily grasped when the data are presented pictorially, the simplest form of which is the histogram. More usually the plot is of cumulative percentage oversize or undersize against particle diameters, or percentage frequency against particle diameters. It is common to use a weight basis for percentage but surface or number may, in some cases, be more relevant. The basis of percentage; weight, surface, or volume should be specified, together with the basis of diameter; sieve, Stokes, or otherwise. The measuring procedure should also be noted.

Figure 20-1 presents the data from Table 20-1 in both cumulative and frequency format. In order to smooth out experimental errors it is best to generate the frequency curve from the slope of the cumulative curve, to use wide-size intervals or a data-smoothing computer program. The advantage of this method of presenting frequency data is that the area under the frequency curve equals 100 percent, hence, it is easy to visually compare similar data. A typical title for such a presentation would be: *Relative and cumulative mass distributions of quartz powder by pipet sedimentation.*

An alternative presentation of the same data is given in Fig. 20-2. In this case the sizes on the abscissa are in a logarithmic progression [log (x)] and the frequency is $[dP/d \ln (x)]$ so that the area under the frequency curve is, again, 100. This form of presentation is useful for wide-size distributions: Many instrument software programs generate data in a logarithmic-size interval and information is compressed in the finer-size intervals if an arithmetic-size progression is used.

It is always preferable to plot data so that the area under the frequency curve is normalized to 100 percent since this facilitates data comparison.

Particle-Size Equations It is common practice to plot size-distribution data in such a way that a straight line results, with all the advantages that follow from such a reduction. This can be done if the curve fits a standard law such as the normal probability law. According to the normal law, differences of equal amounts in excess or deficit from a mean value are equally likely. In order to maintain a symmetrical bell-shaped curve for the frequency distribution it is necessary to plot the population density (e.g., percentage per micron) against size.

With the **log-normal probability law,** it is ratios of equal amounts which are equally likely. In order to obtain a symmetrical bell-shaped frequency curve it is therefore necessary to plot the population density per log (micron) against log (size) [Hatch and Choate, *J. Franklin Inst.,* **207,** 369 (1929)]:

$$Y = \text{erf}\left(\frac{\ln (X/X')}{\sigma}\right) \tag{20-1}$$

Other equations in general use include the Gates-Gaudin-Schumann [Schumann, *Am. Inst. Min. Metall. Pet. Eng.,* Tech. Paper 1189, Min. Tech. (1940)]:

$$Y = (X/k)^m \tag{20-2}$$

The Rosin-Rammler-Bennett [Rosin and Rammler, *J. Inst. Fuel,* **7,** 29–36 (1933); Bennett, ibid., **10,** 22–29 (1936)]:

$$Y = 1 - [\exp\{-(X/X')^n\}] \tag{20-3}$$

The Gaudin-Meloy [Gaudin and Meloy, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **223,** 40–50 (1962)]:

$$Y = 1 - \left[1 - \left(\frac{X}{X'}\right)\right]^r \tag{20-4}$$

where Y = cumulative fraction by weight undersize; x = size; k, X' = parameters with dimensions of size, m, n, r = dimensionless exponents; erf = normal probability function; and σ = standard deviation parameter.

The Rosin-Rammler is useful for monitoring grinding operations for highly skewed distributions, but should be used with caution since the device of taking logs always reduces scatter, hence taking logs twice is not to be recommended. The Gates-Gaudin-Schumann has the advantage of simplicity and the Gaudin-Meloy can be fitted to a variety of distributions found in practice. The log-normal distribution

TABLE 20-1 Tabular Presentation of Particle Size Data

Particle size in microns (x)	Percentage undersize (P)	Percentage per micron $\left(\frac{dP}{dx}\right)$	Percentage per log (micron) $\frac{dP}{d \log (x)}$	Particle size in microns (x)	Percentage undersize (P)	Percentage per micron $\left(\frac{dP}{dx}\right)$	Percentage per log (micron) $\frac{dP}{d \log (x)}$
2.5	0.00	0.000	0.00	52.5	97.41	0.425	13.21
7.5	0.29	0.058	0.12	57.5	98.59	0.236	8.16
12.5	5.06	0.953	3.21	62.5	99.24	0.130	4.92
17.5	19.44	2.875	15.54	67.5	99.59	0.071	2.92
22.5	39.93	4.098	34.68	72.5	99.79	0.039	1.71
27.5	59.68	3.951	47.97	77.5	99.89	0.021	1.00
32.5	74.91	3.047	48.92	82.5	99.95	0.012	0.58
37.5	85.18	2.054	41.04	87.5	99.98	0.006	0.34
42.5	91.55	1.273	30.31	92.5	100.00	0.004	0.20
47.5	95.28	0.748	20.58			0.000	0.12

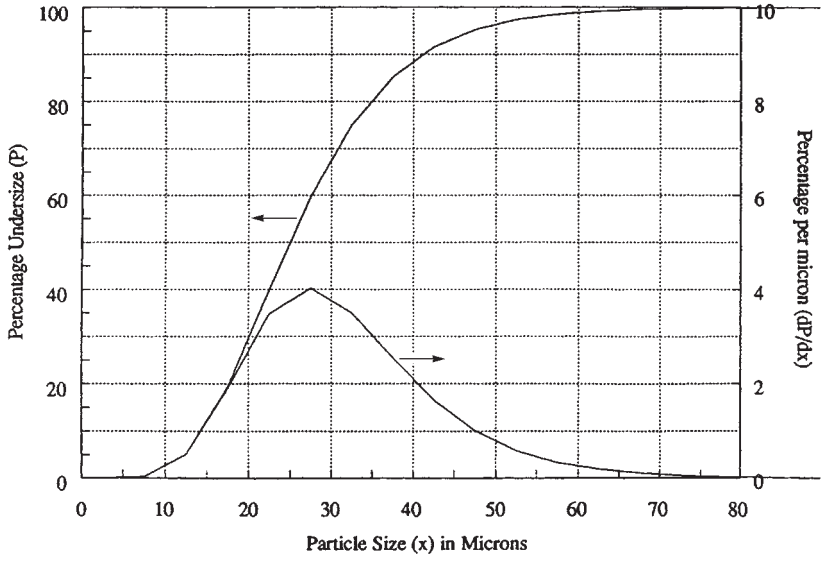


FIG. 20-1 Particle-size distribution curve plotted on linear axes.

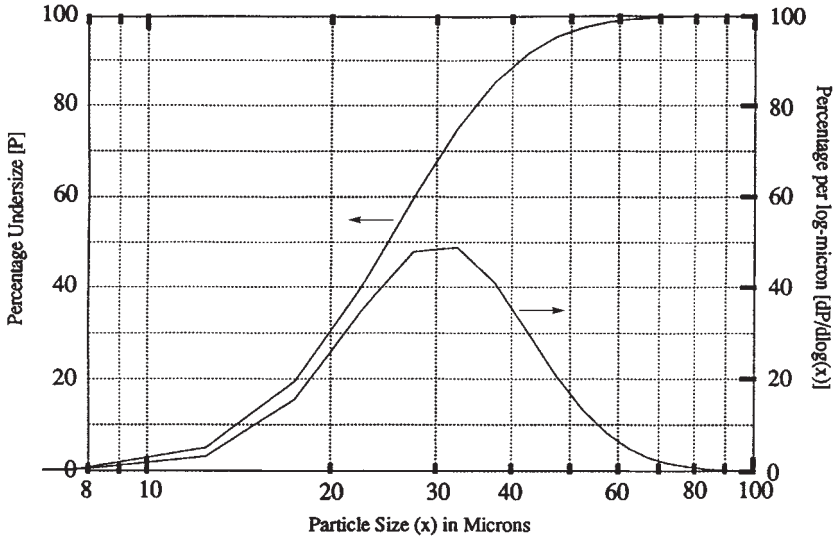


FIG. 20-2 Particle-size distribution curve plotted using a logarithmic scale for the abscissa.

has an advantage in that transformations between distributions is simple; that is, if the number distribution is log-normal, the surface and volume distributions are also log-normal with the same slope (σ).

Average Particle Size A powder has many average sizes; hence it is essential that they be well specified. The median is the 50 percent size; half the distribution is coarser and half finer. The mode is a high-density region; if there is more than one peak in the frequency curve, the distribution is said to be multimodal. The mean is the center of gravity of the distribution. The center of gravity of a mass (volume) distribution is defined by: $X_{VM} = \sum XdV/\sum dV$ where $dV = X^3dN$: dV is the volume of dN particles of size X. This is defined as the *volume-moment mean diameter* and differs from the mean for a number or surface distribution.

Specific Surface This can be calculated from size distribution data. For example, the Gates diagram employs a plot of cumulative percent by weight undersize versus reciprocal diameter; the area beneath the curve represents surface. Likewise the area under the Roller diagram of weight percent per micron against log of diameter represents surface (Work and Whitby, op.cit., p 477).

Sampling of Powders An important prerequisite to accurate particle size analysis is proper powder sampling. Powders may be classified as nonsegregating (cohesive) or segregating (free-flowing). Representative samples are more easily taken from cohesive powders *provided* they have previously been mixed. It is difficult to mix free-flowing powders; hence it is advisable to sample them in motion. (1) A powder should always be sampled when in motion. (2) The whole of the stream of powder should be taken for many short increments of time in preference to part of the stream being taken for the whole of the time. The estimated maximum sample errors on a 60:40 blend of free-flowing sand using different sampling techniques are given in Table 20-2.

TABLE 20-2 Reliability of Selected Sampling Methods

Method	Estimated maximum sample error
Cone and quartering	22.7%
Scoop sampling	17.1%
Table sampling	7.0%
Chute splitting	3.4%
Spinning riffling	0.42%

The spinning riffler obeys the "Golden Rules of Sampling" given above and, therefore, generates the most representative samples [Allen and Khan, *The Chemical Engineer,* 103–112 (May 1970)]. In this device (Fig. 20-3) a ring of containers rotates under the powder feed. If the powder flows for a long time compared with the period of rotation (a ratio of at least 30:1), the sample in each container will be made up of many small portions drawn from all parts of the bulk. Several different configurations of this device are available for both cohesive and free-flowing powders. In the one illustrated, a single pass divides the bulk into 16 parts, two passes increases this subdivision to 256:1, and so on.

PARTICLE-SIZE MEASUREMENT

There are many techniques available for measuring the particle-size distribution of powders. The wide size range covered, from nanometers to millimeters, cannot be analyzed using a single measurement principle. Added to this are the usual constraints of capital costs versus running costs, speed of operation, degree of skill required, and, most important, the end-use requirement.

If the particle-size distribution of a powder composed of hard, smooth spheres is measured by any of the techniques, the measured values should be identical. However, there are many different size distributions that can be defined for any powder made up of nonspherical particles. For example, if a rod-shaped particle is placed on a sieve, its diameter, not its length, determines the size of aperture through which it will pass. If, however, the particle is allowed to settle in a viscous fluid, the calculated diameter of a sphere of the same substance that would have the same falling speed in the same fluid (i.e., the Stokes diameter) is taken as the appropriate size parameter of the particle.

Since the Stokes diameter for the rod-shaped particle will obviously differ from the rod diameter, this difference represents added information concerning particle shape. The ratio of the diameters measured by two different techniques is called a **shape factor.**

Heywood [Heywood, *Symposium on Particle Size Analysis,* Inst. Chem. Engrs. (1947), Suppl. 25, 14] recognized that the word "shape" refers to two distinct characteristics of a particle—form and proportion. The first defines the degree to which the particle approaches a definite form such as cube, tetrahedron, or sphere, and the second by the relative proportions of the particle which distinguish one cuboid, tetrahedron, or spheroid from another in the same class. He replaced historical qualitative definitions of shape by numerical shape coefficients.

Gravitational Sedimentation Methods In gravitational sedimentation methods, particle size is determined from settling velocity and undersize fraction by changes of concentration in a settling suspension. The equation relating particle size to settling velocity is known as Stokes law:

$$d_{St} = \sqrt{\frac{18\eta u}{(\rho_s - \rho_f)g}} \tag{20-5}$$

where d_{St} is the Stokes diameter, η is viscosity, u is particle settling velocity under gravity, ρ_s is the particle density, ρ_f is the fluid density, and g is the acceleration due to gravity.

Stokes diameter is defined as the diameter of a sphere having the same density and the same velocity as the particle in a fluid of the same density and viscosity settling under laminar flow conditions. Correction for deviation from Stokes law may be necessary at the large end of the size range. Sedimentation methods are limited to sizes above a μm due to the onset of thermal diffusion (Brownian motion) at smaller sizes.

An experimental problem is to obtain adequate dispersion of the particles before sedimentation analysis. For powders that are difficult to disperse the addition of dispersing agents is necessary, together with ultrasonic probing. It is essential to examine a sample of the dispersion under a microscope to ensure that the sample is fully dispersed.

Equations to calculate size distributions from sedimentation data are based on the assumption that the particles fall freely in the suspension. In order to ensure that particle-particle interaction does not prevent free fall, an upper-volume concentration limit of around 0.2 percent is recommended.

There are various procedures available for determining the changing solids concentration of a sedimenting suspension:

In the *pipet method,* concentration changes are monitored by extracting samples from a sedimenting suspension at known depths of fall and predetermined times. The method is best known as the Andreasen modification [Andreasen, *Kolloid-Z.,* **49,** 253 (1929)] shown in Fig. 20-4. Two 10-mL samples are withdrawn from a fully dispersed, agitated suspension at zero time to corroborate the 100 percent concentration given by the known weight of powder and volume of liquid making up the suspension. The suspension is then allowed to settle, and 10-mL samples are taken at time intervals in a geometric 2:1 time progression starting at 1 minute (i.e., 1, 2, 4, 8, 16, 32, 64 minutes); if longer time intervals than this are used it is necessary to enclose the pipet in a temperature-controlled environment. The amounts of powder in the extracted samples are determined by

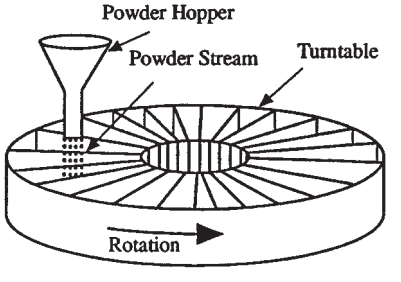


FIG. 20-3 Spinning riffler sampling device.

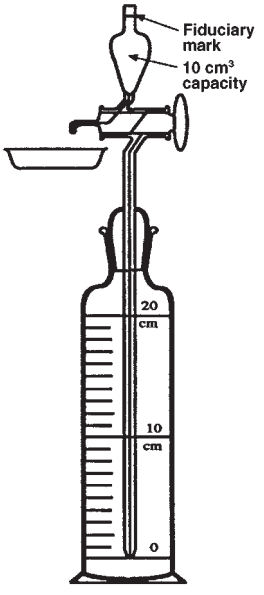


FIG. 20-4 Equipment used in the pipet method of size analysis.

drying, cooling in a dessicator, and weighing. Stokes diameters are determined from the predetermined times and the depths, with correction for the changes in depth due to the extractions. The cumulative, mass, undersize distribution comprises a plot of the normalized concentration against the Stokes diameter. A reproducibility of ±2 percent is possible using this apparatus. The technique is versatile in that it is possible to analyze most powders which are dispersible in liquids; its disadvantages are that it is a labor-intensive procedure and a high level of skill is needed.

The *hydrometer method* is simpler in that the density of the suspension, which is related to the concentration, is read directly from the stem of the hydrometer while the depth is determined by the distance of the hydrometer bulb from the surface (ASTM Spec. Pub. 234, 1959). The method has low resolution but is widely used in soil science studies.

In *gravitational photosedimentation methods* the changing concentration with time and depth of fall is monitored using a light beam. These methods give a continuous record of changing optical density with time and depth and have the added advantage that the beam can be scanned to the surface to reduce the measurement time. A correction needs to be applied to compensate for the breakdown in the laws of geometric optics (due to diffraction effects the particles cut off more light than geometric optics predicts). The normalized measurement is a cumulative surface undersize.

In *gravitational X-ray sedimentation methods* the changing concentration with time and depth of fall is monitored using an X-ray beam. These methods give a continuous record of changing X-ray density with time and depth and have the added advantage that the beam can be scanned to the surface to reduce the measurement time. The method is limited to materials having a high atomic mass (i.e., X-ray opaque material) and gives a mass undersize distribution directly.

Sedimentation Balance Methods In sedimentation balances the weight of sediment is measured as it accumulates on a balance pan suspended in an initially homogeneous suspension. The technique is slow because of the time required for the smallest fine particle to settle out over a given column height. The relationship between settled weight (P), weight undersize (W) and time (t) is given by the following equation.

$$P = W - \frac{dP}{d \ln (t)} \tag{20-6}$$

Centrifugal Sedimentation Methods These methods extend sedimentation methods into the submicron size range. Sizes are calculated from a modified version of Stokes equation:

$$d_{St} = \sqrt{\frac{18\eta u}{(\rho_s - \rho_f)\omega^2 r}} \tag{20-7}$$

where r is the measurement radius and ω is the radial velocity of the centrifuge. The concentration calculations are complicated due to radial dilution effects (i.e., particles do not travel in parallel paths as in gravitational sedimentation but move away from each other as they settle radially outwards).

Particle velocities are given by:

$$u = \frac{\ln\left(\frac{r}{s}\right)}{t} \tag{20-8}$$

where both r, the measurement radius, and s, the surface radius can be varying; the former varies if the system is a scanning system, and the latter if the surface falls due to the extraction of samples.

Concentration undersize D_m is determined using Kamack's equation [Kamack, *Br. J. Appl. Phys.*, **5,** 1962–68 (1972)]:

$$Q(D_m) = \int_0^{D_m} \left(\frac{r_i}{s_i}\right)^2 f(D) dD \tag{20-9}$$

where r_i is the measurement radius and s_i is the surface radius, either or both of which may vary during the analysis. $f(D)dD = F(D)$ is the fraction of particles in the narrow-size range dD. $(r_i/s_i)^2$ is the radial dilution correction factor.

The disc centrifuge, developed by Slater and Cohen and modified by Allen and Svarovsky [Allen and Svarovsky, *Dechema Monogram,* Nuremberg, Numbers 1589–1615, 279–292 (1975)], is essentially a centrifugal pipet device. Size distributions are calculated from the measured solids concentrations of a series of samples withdrawn through a central drainage pillar at various time intervals.

In the centrifugal disc photosedimentometer concentration changes are monitored by a light beam. In one high-resolution mode of operation, the suspension under test is injected into clear fluid in the spinning disc through an entry port, and a layer of suspension is formed over the free surface of the liquid (the line-start technique). The analysis can also be carried out using a homogeneous suspension. Very low concentrations are used, but the light-scattering properties of small particles make it difficult to interpret the measured data.

Several centrifugal cuvet photocentrifuges are commercially available. These instruments use the same theory as the disc photocentrifuges but are limited in operation to the homogeneous mode of operation.

The X-ray disc centrifuge is a centrifugal version of the gravitational instruments and extends the measuring technique well into the sub-μm-size range.

Microscope Methods In microscope methods of size analysis, direct measurements are made on enlarged images of the particles. In the simplest technique, linear measurements of particles are made by using a calibrated scale on top of the particle image. Alternatively, the projected areas of the particles can be compared to areas of circles.

Feret's diameter (Fig. 20-5) is the perpendicular projection, in a fixed direction, of the tangents to the extremities of the particle profile. **Martin's diameter** is a line, parallel to a fixed direction, which divides the particle profile into two equal areas. Since the magnitude of these statistical diameters varies with particle orientation, these diameters have meaning only when a sufficient number of measurements are averaged.

Quantitative image microscopy has revolutionized microscopic methods of size and shape analysis. The sizes of large numbers of particles can be rapidly determined and the data manipulated. The speed and sophistication of such devices make it possible to devise new methods for characterizing the shape of fine particles. In **Fourier techniques** the shape characteristic is transformed into a signature waveform. Beddow and coworkers (Beddow, *Particulate Science and Technology,* Chemical Publishing, New York, 1980) take the particle centroid as a reference point. A vector is then rotated about this centroid with the tip of the vector touching the periphery. A plot of the magnitude of the vector against its angular position is a wave-type function. This wave form is then subjected to Fourier analysis. The lower frequency harmonics constituting the complex wave correspond to the gross external morphology, whereas the higher frequencies correspond to the texture of the fine particle. **Fractal logic** was introduced into fine-particle science by Kaye and coworkers [Kaye, op. cit. (1981)], who show that the non-Euclidean logic of Mandelbrot can be applied to describe the ruggedness of a particle profile. A combination of fractal dimension, and geometric-shape factors such as aspect ratio, can be used to describe a population of fine particles of various shapes, and these can be related to the functional properties of the particle.

Stream Scanning Methods In these techniques, the particles to be measured are examined individually in a stream of fluid. As the particles pass through a sensing zone they are counted and measured through their interaction with the sensor. It is essential to use very low particle concentrations since the signals received from two particles is indistinguishable from the signal received from a single larger particle.



FIG. 20-5 Statistical (Martin's and Feret's) and projected area diameters for an irregular particle.

In the **electrical sensing zone method** a dilute well-dispersed suspension in an electrolyte is caused to flow through a small aperture [Kubitschek, *Research,* **13,** 129 (1960)]. The changes in the resistivity between two electrodes on either side of the aperture, as the particles pass through, are directly related to the volumes of the particles. The pulses are fed to a pulse-height analyzer where they are counted and scaled. The method is limited by the pulse-height analyzer which can resolve pulses in the range 16,000:1 (i.e., a volume diameter range of about 25:1) and the need to suspend the particles in an electrolyte.

In **light blockage methods** the size of the particle is determined from the amount of light blocked off by the particle as it passes through a sensing zone. In **light scattering methods** the particle size is determined either from the light scattered in the forward direction or at some angle, usually 90° from the direction of the incident beam. The light source can be incandescent or laser and the detecting mechanism ranges from simple photodetectors to parabolic mirrors. The particles can be suspended in a liquid or gas.

In the Lasentec instruments a chord-length distribution is generated, from a rotating infrared beam, and this is converted to a size distribution. Since highly concentrated systems can be interrogated this system can be used for on-line size analysis.

Field Scanning Methods In these techniques, the particles to be measured are examined collectively, and the signal from the assembly of particles is deconvulated to generate a size distribution.

Light Diffraction Methods These comprise one of several field scanning procedures in which an assembly of particles is irradiated with a laser beam. The forward light-scattered flux contains information on the size distribution of the particles. Several assumptions are made in the transformation of the diffraction pattern into particle-size data, and the various companies manufacturing these instruments offer different interpretive programs. The dozen or so instruments currently marketed tend to disagree with each other and also generate a wider distribution than other methods. Their advantages are ease of use and high reproducibility. Although low-angle laser light scattering is only applicable down to around 0.7 μm, the lower limit can be extended using secondary measurements of 90 degree scattering of white light, polarization ratio, and so on.

The principle of ultrasonic attenuation is that plane sound waves moving through a slurry are attenuated according to the size and concentration of the particles in the slurry. Two instruments have been described, one for sizing in the plus-one μm up to mm sizes (Reibel and Loffler, *European Symposium on Particle Characterization,* Nuremberg, Germany, publ. Nuremberg Messe, 1989) and the other for sub-μm sizing (Alba, US Patent 5121629, June 16, 1992). Although in its infancy, the technique shows high promise for on-line size analysis at high-volume (+50%) concentrations.

Photon Correlation Spectroscopy (PCS) The size distribution of particles ranging in size from a few nanometers to a few μm can be determined from their random motion due to molecular bombardment. This technique involves passing a laser beam into a suspension and measuring the Doppler shift of the frequency of light scattered at an angle (usually 90 degrees) with respect to the incident beam. The Doppler shift is related to particle velocity which, in turn, is inversely related to their size. Multiangle instruments are also available to generate the angular variation of scattered light intensity for derivation of molecular weight, radius of gyration, translational and rotational diffusion coefficients, and other molecular properties.

Through dynamic light scattering in the controlled reference method, a laser beam is fed into an agitated measuring cell or flowing suspension using an optical-wave guide. Particles within 50 microns of the tip of the wave guide (a fiber-optic probe) scatter light some of which is reflected back into the fiber and transmitted back through the guide. The reflected light from the interface between the guide tip and the suspension is also transmitted back. If these two components are coherent they will interfere with each other and result in a component of signal which has the difference or "beat" frequency between the reflected and scattered components. The difference frequencies are the same as the desired Doppler shifts. The received signal resembles random noise at the output of the silicon photodiode as a result of the mixing of the Doppler shifts from all the particles scattering the laser light. The photodiode output is digitized and the power spectrum of the signal is determined using Fast Fourier Transform techniques. The spectrum is then analyzed to determine the particle-size distribution. Two instruments based on this phenomenon are available, the Microtrac UPA (Fig. 20-6) [Trainer, Freud, and Weiss, *Pittsburgh Conference, Analytical and Applied Spectroscopy* Symp. Particle Size Analysis (March 1990)] and the Malvern Hi-C which operates in a similar manner to cover the size range 0.015 μm to 1 μm at concentrations from 0.01 to 50 percent solids.

Sieving Methods and Classification Sieving is probably the most frequently used and abused method of analysis because the equipment, analytical procedure, and basic concepts are deceptively simple. In sieving, the particles are presented to equal-size apertures that constitute a series of go-no-go gauges. Sieve analysis presents three major difficulties: (1) with woven-wire sieves, the weaving process produces three-dimensional apertures with considerable tolerances, particularly for fine-woven mesh; (2) the mesh is easily damaged in use; (3) the particles must be efficiently presented to the sieve apertures.

Sieves are often referred to by their mesh size, which is the number of wires per linear unit. The U.S. Standard Sieve Series as described by the American Society of Testing and Materials (ASTM) document E-11-87 *Standard Specification for Wire-cloth Sieves for Testing Purposes* addresses sieve opening sizes from 20 μm (635 mesh) to 125 mm (5.00 in). Electroformed sieves with square or round apertures and tolerances of ±2 μm, are also available.

For coarse separation **dry sieving** is used, but other procedures are necessary as the powder becomes finer and more cohesive. Machine sieving is performed by stacking sieves in ascending order of aperture size and placing the powder on the top sieve. The most aggressive action is performed with Pascal Inclyno and Tyler Ro-tap sieves which combine a gyratory and jolting movement, although a simple vibratory action may be suitable in many cases. With the Air-Jet sieve a rotating jet below the sieving surface cleans the apertures and helps the passage of fines through the apertures. The sonic sifter combines two actions, a vertically oscillating column of air, and a repetitive mechanical pulse. Wet sieving is frequently used with cohesive powders.

Elutriation Methods and Classification In gravity elutriation the particles are classified, in a column, by a rising fluid current. In centrifugal elutriation the fluid moves inward against the centrifugal force. A *cyclone* is a centrifugal elutriator, though not usually so regarded (see Sec. 17: "Dust Collection Equipment"). The cyclosizer is a series of inverted cyclones with added apex chambers through which water flows. Suspension is fed into the largest cyclone and particles are separated into different size ranges.

Surface Area Determination The surface-to-volume ratio is an important powder property since it governs the rate at which a powder interacts with its surroundings. Surface area may be determined from size-distribution data or measured directly by flow through a powder bed or the adsorption of gas molecules on the powder surface. Other methods such as gas diffusion, dye adsorption from solution, and heats of adsorption have also been used. It is emphasized that a powder does not have a unique surface, unless the surface is considered to be absolutely smooth, and the magnitude of the measured surface depends upon the level of scrutiny (e.g., the smaller the gas molecules used for gas adsorption measurement the larger the measured surface).

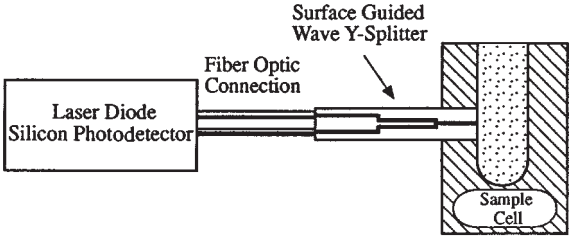


FIG. 20-6 Diagram of the Leeds and Northrup Ultrafine Particle Analyzer (UPA).

Gas adsorption is the preferred method of surface-area determination. An isotherm is generated of the amount of gas adsorbed against gas pressure, and the amount of gas required to form a monolayer is determined. The surface area can then be calculated using the cross-sectional area of the gas molecule. Outgassing of the powder before analysis should be conducted very carefully to ensure reproducibility. Commonly, nitrogen at liquid nitrogen vapor pressure is used but, for low surface-area powders, the adsorbed amounts of krypton or xenon are more accurately found. Many theories of gas adsorption have been advanced, but measurements are usually interpreted by using the BET theory [Brunauer, Emmett, and Teller, *J. Am. Chem. Soc.,* **60,** 309 (1938)].

In the **static method** the powder is isolated under high vacuum and surface gases driven off by heating the container. The container is next immersed in liquid nitrogen and known amounts of nitrogen vapor are admitted into the container at measured increasing pressures in the relative pressure range 0.05 to 0.35.

In the **dynamic method** the powder is flushed with an inert gas during degassing, nitrogen is then adsorbed on the powder in a carrier of helium gas at known relative pressure while the powder is in a container surrounded by liquid nitrogen. The changing concentration of nitrogen is measured by a calibrated conductivity cell so that the amount adsorbed can be determined.

Permeametry The flow of fluid through a packed bed of powder can be related to the surface area of the powder using the Carman-Arnel Equation [Carman and Arnell, *Can. J. Res.,* **26,** 128 (1948)]. Flow takes place through two mechanisms, viscous and diffusional flow. The latter term is often neglected leading to erroneous results [British Standard BS 4359: Part 2: (1982) *Determination of specific surface of powders. Recommended air permeability methods*]. Essentially, the pressure drop across the bed is directly related to the flow rate through it, and the constant of proportionality includes surface area. The assumptions made in deriving the equation are so sweeping that the derived value is better considered as a surface-related parameter.

On-line Procedures The growing trend toward automation in industry has resulted in many studies of rapid procedures for generating size information so that feedback loops can be instituted as an integral part of a process. Many of these techniques are modifications of more traditional methods. The problems associated with on-line methods include: allocation and preparation of a representative sample; analysis of the sample; evaluation of the results. The interface between the measuring apparatus and the process has the potential of high complexity, and consequently, high costs [Leschonski, *Particle Characterization,* **1,** 1 (July 1984)].

PRINCIPLES OF SIZE REDUCTION

General References: Annual reviews of size reduction, *Ind. Eng. Chem.,* October or November issues, by Work from 1934 to 1965, by Work and Snow in 1966 and 1967, and by Snow in 1968, 1969, and 1970; and in *Powder Technol.,* **5,** 351 (1972), and **7** (1973); Snow and Luckie, **10,** 129 (1973), **13,** 33 (1976), **23**(1), 31 (1979). *Chemical Engineering Catalog,* Reinhold, New York, annually. Cremer-Davies, *Chemical Engineering Practice,* vol. 3: *Solid Systems,* Butterworth, London, and Academic, New York, 1957. *Crushing and Grinding: A Bibliography,* Chemical Publishing, New York, 1960. *European Symposia on Size Reduction:* 1st, Frankfurt, 1962, publ. 1962, Rumpf (ed.), Verlag Chemie, Düsseldorf; 2d, Amsterdam, 1966, publ. 1967, Rumpf and Pietsch (eds.), *DECHEMA-Monogr.,* **57;** 3d, Cannes, 1971, publ. 1972, Rumpf and Schönert (eds.), *DECHEMA-Monogr.,* **69.** Gaudin, *Principles of Mineral Dressing,* McGraw-Hill, New York, 1939. International Mineral Processing Congresses: *Recent Developments in Mineral Dressing,* London, 1952, publ. 1953, Institution of Mining and Metallurgy; *Progress in Mineral Dressing,* Stockholm, 1957, publ. London, 1960, Institution of Mining and Metallurgy; 6th, Cannes, 1962, publ. 1965, Roberts (ed.), Pergamon, New York; 7th, New York, 1964, publ. 1965, Arbiter (ed.), vol. 1: *Technical Papers,* vol. 2: *Milling Methods in the Americas,* Gordon and Breach, New York; 8th, Leningrad, 1968; 9th, Prague, 1970; 10th, London, 1973; 11th, Cagliari, 1975; 12th, São Paulo, 1977. Lowrison, *Crushing and Grinding,* CRC Press, Cleveland, 1974. *Pit and Quarry Handbook,* Pit & Quarry Publishing, Chicago, 1968. Richards and Locke, *Text Book of Ore Dressing,* 3d ed., McGraw-Hill, New York, 1940. Rose and Sullivan, *Ball, Tube and Rod Mills,* Chemical Publishing, New York, 1958. Snow, *Bibliography of Size Reduction,* vols. 1 to 9 (an update of the previous bibliography to 1973, including abstracts and index), U.S. Bur. Mines Rep. SO122069, available IIT Research Institute, Chicago, Ill. 60616. Stern, "Guide to Crushing and Grinding Practice," *Chem. Eng.,* **69**(25), 129 (1962). Taggart, *Elements of Ore Dressing,* McGraw-Hill, New York, 1951.

Since a large part of the literature is in the German language, availability of English translations is important. Translation numbers cited in this section refer to translations available through the National Translation Center, Library of Congress, Washington, DC. Also, volumes of selected papers in English translation are available from the Institute for Mechanical Processing Technology, Karlsruhe Technical University, Karlsruhe, Germany.

PROPERTIES OF SOLIDS

Grindability is a measure of the rate of grinding of material in a particular mill (discussed later).

Single-Particle Fracture More fundamental knowledge of the breaking action occurring within mills depends on developing knowledge of the mechanism of single-particle fracture. The early workers [Smekal, *Z. Ver. Dtsch. Ing. Beh. Verfahrenstech.,* no. 6, 159–165 (1938), NTC translation 70-14798; and Smekal *Z. Ver. Dtsch. Ing.,* **81**(46), 1321–1326 (1937), NTC translation 70-14799] investigated the breakage of cubes. This gives misleading results when cubes are crushed between platens because surface irregularities concentrate the load and give nonuniform load distribution. More meaningful measurements can be made with spheres, which approximate the shapes of particles broken in mills.

The force required to crush a single particle that is spherical near the contact regions is given by the equation of Hertz (Timoschenko and Goodier, *Theory of Elasticity,* 2d ed., McGraw-Hill, New York, 1951).

In an experimental and theoretical study on glass spheres Frank and Lawn [*Proc. R. Soc.* (*London*), **A299**(1458), 291 (1967)] observed the repeated formation of ring cracks as increasing load was applied, causing the circle of contact to widen. Eventually a load is reached at which the crack deepens to form a cone crack, and at a sufficient load this propagates across the sphere to cause breakage into fragments. The authors' photographs show how the size of flaws that happen to be encountered at the edge of the circle of contact can result in a distribution of breakage strengths. Thus the mean value of breakage strength depends partly on intrinsic strength and partly on the extent of flaws present. From the measured breaking load and the Hertz theory one can calculate the apparent tensile strength σ_0, which is the maximum stress under the circle of contact normal to the direction of crack propagation. This tensile strength is the most appropriate one to use for breakage in mills, although the crushing strength of cubes still is often used as a rule of thumb. The propagation of cracks across spheres and disks has been recorded by high-speed spark cinematographs by Rumpf et al. (*Second European Symposium on Size Reduction,* op. cit., 1966, p. 57). They attempt to extend the Hertz theory deeper into the sphere although it is not valid far from the point of load application. The stress at points within the sphere far from the point of load application is given by the Bousinesque theory [Sternberg and Rosenthal, *J. Appl. Mech.,* **12,** 413 (1952); and Hiramatsu and Oka, *Int. J. Rock Mech. Min. Sci.,* **3,** 89 (1966)].

Snow and Paulding (Heywood Memorial Conference, Loughborough University, England, September 1973) observed that when breakage occurs, the finest fragments arise near the circle of contact where the stored internal stress is highest. They postulated that the fragment-size distribution could be calculated by assuming that the local fragment size is correlated with the locally stored stress energy just before fracture occurs. Calculated fragment-size distributions are roughly similar to those that they measured for glass spheres and various hard minerals as well as to distributions measured by Bergstrom and Sollenberger [*Trans. Am. Inst. Min. Metall. Pet. Eng.,* **220,** 373–

379 (1961)]. From this it can be concluded that the wide distribution of fragment sizes from milling is inherent in the breakage process itself and that attempts to improve grinding efficiency by weakening the particles will result in coarser fragments which may require a further break to reach the desired size.

Different mills are designed to apply the force in different ways [Rumpf, *Chem. Ing. Tech.,* **31,** 323–327 (1959), NTC translation 61-12395]. The detailed prediction of grinding rates and product-size distribution from mills awaits the development of a simulation model based on the physics of fracture. An initial attempt is that of Buss and Shubert (*Third European Symposium on Size Reduction,* op. cit., 1972, p. 233), who assume that mill performance is given by the sum of breakage events which are similar to *single-particle breakage experiments* in the laboratory. A paper by Schönert [*Trans. Am. Inst. Min. Metall. Pet. Eng.,* **252**(1), 21 (1972)] summarizes single-particle-breakage data from numerous publications from the Technical University of Karlsruhe, Germany. Hildinger [*Freiberg. Forschungsh.,* **A480,** 19 (1970)] and Steier and Schönert (*Third European Symposium on Size Reduction,* op. cit., 1972, p. 135) report more experimental results on the probability of breakage of single particles by drop-weight experiments.

Grindability Grindability is the amount of product from a particular mill meeting a particular specification in a unit of grinding time e.g., tons per hour passing 200 mesh. The chief purpose of a study of grindability is to evaluate the size and type of mill needed to produce a specified tonnage and the power requirement for grinding. So many variables affect grindability that this concept can be used only as a rough guide to mill sizing; it says nothing about product-size distribution or type or size of mill. If a particular energy law is assumed, then the grinding behavior in various mills can be expressed as an energy coefficient or **work index** (discussed later). This more precise concept is limited by the inadequacies of these laws but often provides the only available information.

The technology based on grindability and energy considerations is being supplanted by computer simulation of milling circuits (see subsection "Simulation of Milling Circuits"), in which the gross concept of grindability is replaced by the **rate of breakage function** (sometimes called the selection function), which is the grindability of each particle size referred to the fraction of that size present.

Factors of hardness, elasticity, toughness, and cleavage are important in determining grindability. Grindability is related to modulus of elasticity and speed of sound in the material [Dahlhoff, *Chem. Ing. Tech.,* **39**(19), 1112–1116 (1967)].

The **hardness** of a mineral as measured by the **Mohs scale** is a criterion of its resistance to crushing [Fahrenwald, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **112,** 88 (1934)]. It is a fairly good indication of the abrasive character of the mineral, a factor that determines the wear on the grinding media. Arranged in increasing order or hardness, the Mohs scale is as follows: 1, talc; 2, gypsum; 3, calcite; 4, fluoride; 5, apatite; 6, feldspar; 7, quartz; 8, topaz; 9, corundum; and 10, diamond.

Materials of hardness 1 to 3 inclusive may be classed as soft; 4 to 7, as intermediate; and the others, as hard. Examples are:

Soft Materials (1) Talc, dried filter-press cakes, soapstone, waxes, aggregated salt crystals; (2) gypsum, rock salt, crystalline salts in general, soft coal; (3) calcite, marble, soft limestone, barites, chalk, brimstone.

Intermediate Hardness (4) Fluorite, soft phosphate, magnesite, limestone; (5) apatite, hard phosphate, hard limestone, chromite, bauxite; (6) feldspar, ilmenite, orthoclase, hornblendes.

Hard Materials (7) Quartz, granite; (8) topaz; (9) corundum, sapphire, emery; (10) diamond.

A hardness classification of stone based on the **compressive strength** of 1-in cubes is as follows, for loadings in pounds-force per square inch: very soft, 10,000; soft, 15,000; medium, 20,000; hard, 25,000; very hard, 30,000.

Grindability Methods Laboratory experiments on single particles have been used to correlate grindability. In the past it has usually been assumed that the total energy applied could be related to the grindability whether the energy is applied in a single blow or by repeated dropping of a weight on the sample [Gross and Zimmerly, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **87,** 27, 35 (1930)]. In fact, the results depend on the way in which the force is applied (Axelson, Ph.D. thesis, University of Minnesota, 1949). In spite of this, the results of large mill tests can often be correlated within 25 to 50 percent by a simple test, such as the number of drops of a particular weight needed to reduce a given amount of feed to below a certain mesh size.

Two methods having particular application for coal are known as the ball-mill and Hardgrove methods. In the ball-mill method, the relative amounts of energy necessary to pulverize different coals are determined by placing a weighed sample of coal in a ball mill of a specified size and counting the number of revolutions required to grind the sample so that 80 percent of it will pass through a No. 200 sieve. The grindability index in percent is equal to the quotient of 50,000 divided by the average of the number of revolutions required by two tests (ASTM designation D-408).

In the **Hardgrove method** a prepared sample receives a definite amount of grinding energy in a miniature ball-ring pulverizer. The unknown sample is compared with a coal chosen as having 100 grindability. The Hardgrove grindability index = $13 + 6.93W$, where W is the weight of material passing the No. 200 sieve (see ASTM designation D-409).

Chandler [*Bull. Br. Coal Util. Res. Assoc.,* **29**(10), 333; (11), 371 (1965)] finds no good correlation of grindability measured on 11 coals with roll crushing and attrition, and so these methods should be used with caution. The Bond grindability method is described in the subsection "Capacity and Power Consumption."

Manufacturers of various types of mills maintain laboratories in which grindability tests are made to determine the suitability of their machines. When grindability comparisons are made on small equipment of the manufacturers' own class, there is a basis for scale-up to commercial equipment. This is better than relying on a grindability index obtained in a ball mill to estimate the size and capacity of different types such as hammer or jet mills.

OPERATIONS

Mill Wear Wear of mill components costs nearly as much as the energy required for comminution, hundreds of millions of dollars a year. The finer stages of comminution result in the most wear, because the grinding effort is greatest, as measured by the energy input per unit of feed. Parameters that affect wear fall under three categories: (1) the ore, including hardness, presence of corrosive minerals, and particle size; (2) the mill, including composition, microstructure and mechanical properties of the material of construction, size of mill, and mill speed; and (3) the environment, including water chemistry and pH, oxygen potential, slurry solids content, and temperature [Moore et al., *International J. Mineral Processing,* **22,** 313–343 (1988)].

An abrasion index in terms of kilowatthour input per pound of metal lost furnishes a useful indication. Rough values are quoted in Table 20-3.

The use of hard-surfacing techniques by welding and by inserts has contributed greatly to better maintenance and lower downtime [Lutes and Reid, *Chem. Eng.,* **63**(6), 243 (1956)].

In *wet grinding* a synergy between mechanical wear and corrosion results in higher metal loss than with either mechanism alone [Iwasaki, *International J. Mineral Processing,* **22,** 345–360 (1988)]. This is due to removal of protective oxide films by abrasion, and by increased corrosion of stressed metal around gouge marks (Moore, loc. cit.). Wear rate is higher at lower solids content, since ball coating at high solids protects the balls from wear. This indicates that the mechanism is different from dry grinding. The rate without corrosion can be measured with an inert atmosphere such as nitrogen in the mill. Insertion of marked balls into a ball mill best measures the wear rate at conditions in industrial mills, so long as there is not a galvanic effect due to a different composition of the balls. The mill must be cleared of dissimilar balls before a new composition is tested. Sulfide ores promote corrosion due to galvanic coupling by a chemical reaction with oxygen present. Increasing the pH generally reduces corrosion.

The use of harder materials enhances wear resistance, but this conflicts with achieving adequate ductility to avoid catastrophic brittle failure, so these two effects must be balanced. Wear-resistant materials can be divided into three groups: (1) abrasion-resistant steels, (2)

TABLE 20-3 Abrasion Index Test Results*

Material	Number tested	Product diameter, μm	Work index E_i	Average abrasion index† A_i
Alnico	1			0.3850
Alumina	6	15,500		0.6447
Asbestos cement pipe	1	13,330		0.0073
Cement clinker	2	12,100	10.9	0.0409
Cement raw material	4		10.5	0.0372
Chrome ore	1	10,200	9.6	0.1200
Coke	1		20.7	0.3095
Copper ore	12	12,900	11.2	0.0950
Coral rock	1			0.0061
Diorite	1		19.4	0.2303
Dolomite	5		11.3	0.0160
Gneiss	1		20.1	0.5360
Gold ore	2		14.8	0.2000
Granite	11	15,200	14.4	0.3937
Gravel	2		19.0	0.3051
Hematite	3		8.6	0.0952
Iron ore (misc.)	4		5.4	0.0770
Lead zinc ore	3		8.3	0.1520
Limestone	19	13,000	12.1	0.0256
Magnesite	3	14,400	16.8	0.0750
Magnetite	2		10.2	0.2517
Manganese ore	1		17.2	0.1133
Nickel ore	2		11.9	0.0215
Perlite	2			0.0452
Pumice	1		11.9	0.1187
Quartz	7		12.8	0.1831
Quartzite	3		12.2	0.6905
Rare earths	1			0.0288
Rhyolite	2	13,200		0.4993
Schist-biotite	1		23.5	0.1116
Shale	2	11,200	11.2	0.0060
Slag	1		15.8	0.0179
Slate	1		13.8	0.1423
Sulfur	1		11.5	0.0001
Taconite	7		16.2	0.6837
Trap rock	11	14,900	19.9	0.3860
Average		13,250	13.8	0.228

*Allis-Chalmers Corporation.

†Abrasion index is the fraction of a gram weight lost by the standard steel paddle in 1 h of beating 1600 g of ¾- by ½-in particles. The product averages 80 percent passing 13,250 μm.

alloyed cast irons, and (3) nonmetallics [Durman, *International J. Mineral Processing*, **22,** 381–399 (1988)].

Manganese steel, containing 12 to 14 percent manganese and 1 to 1.5 percent carbon, is characterized by its exceptional toughness combined with adequate wear resistance, and enhanced by the austenitic microstructure having the ability to work harden. Although the relatively low yield strength can lead to problems of spreading in service, this can be compensated for by the addition of chromium or molybdenum; or by the use of a lower manganese grade (6–7 percent) also alloyed with up to 1 percent molybdenum. Applications are generally those involving the highest levels of stress, particularly by high-impact loading, such as jaw-crusher elements, gyratory cone-crusher mantles, and primary hammer-mill parts.

For medium- to high-impact applications a wide range of low-alloy steels are produced containing some chromium, molybdenum, phosphorus, and silicon. Economy of manufacture is a benefit for selection of these steels.

Low-alloy steel production falls into two metallurgical types. The traditional approach is heat treatment to produce a pearlitic microstructure. The other is to add sufficient alloying constituents to permit thermal processing to produce a martensitic structure. Typical applications are ball mill liners and grinding balls. Many of these components are consumed in high tonnages, and this combines with metallurgical characteristics to favor production by forging. Low-alloy steel liners, grates, and balls are also produced as castings.

Alloyed white cast irons fall into the second category. This group includes the nickel-chromium grades known as Ni-hards (Durman, loc. cit.). These contain sufficient chromium to ensure solidification as a white cast iron (at least 2 percent), and sufficient nickel (normally at least 4 percent) to induce hardenability and prevent transformation to soft pearlitic iron. Grade 2 Ni-hard contains massive areas of ledeburite carbide within a matrix of austenite and martensite. Ni-hard 2 is a good general-purpose wear-resistant alloy, but is limited due to an inherent low level of toughness attributed to the presence of the carbide phase. It is suited to small-section components involving low-stress abrasion, such as secondary mill liners. Grade 4 Ni-hard typically contains 5 percent nickel and 8 percent chromium. This alloy is heat-treated to a martensitic matrix and has a modified carbide structure which improves toughness. It is more suited to thicker section castings where heat treatment can consistently control structure.

High-chromium cast irons contain between 12 and 30 percent chromium, 1.5 to 3.5 percent carbon, and frequently contain molybdenum and nickel as secondary constituents. They have become standard in most secondary and tertiary dry-grinding applications (Durman, loc. cit.). These alloys form a metastable austenite structure on casting. Subsequent thermal processing forms secondary chromium-carbide particles dispersed through the matrix. This depletes the austenite of alloy content and facilitates transformation to martensite on quenching. The chromium carbide results in a slightly higher level of toughness than Ni-hard, and higher wear resistance because of greater hardness of chromium carbide. Molybdenum may be added to increase hardenability in heavy sections. Elimination of austenite in the structure can improve resistance to spalling, although spalling limits the range of uses. Hardness can range from 52 to 65 Rockwell. For ball mill balls the dry wear rate is often ⅒ that of cast or forged steel. The cost is 2–3 times as great, so there is an economic advantage. In wet grinding, however, the wear rate of chrome alloys is greater, so the cost may not be competitive. For ring-roll mills, high-chromium molybdenum parts have improved wear costs over use of Ni-hard, and also reduced labor costs for maintenance.

Recent nonmetallic developments include natural rubber, polyurethane, and ceramics. Rubber, due to its high resilience, is extremely wear-resistant in low-impact abrasion. It is inert to corrosive wear in mill liners, pipe linings, and screens. It is susceptible to cutting abrasion, so that wear increases in the presence of heavy particles which penetrate, rather than rebound from the wear surface. Rubber can also swell and soften in solvents. Advantages are its low density leading to energy savings, ease of installation, and sound-proofing qualities. Polyurethane has similar resilient characteristics. Its fluidity at the formation stage makes it suitable for the production of the wearing surface of screens, diaphragms, grates, classifiers, and pump and flotation impellers. The low heat tolerance of elastomers limits their use in dry processing where heat may build up.

Ceramics fill a specialized niche in comminution where metallic contamination cannot be tolerated. Therefore ceramics are used for milling cements and pigments. Ceramic tiles have been used for lining roller mills and chutes and cyclones, where there is a minimum of impact.

Safety The explosion hazard of such nonmetallic materials as sulfur, starch, wood flour, cereal dust, dextrin, coal, pitch, hard rubber, and plastics is often not appreciated (Hartmann and Nagy, U.S. Bur. Mines Rep. Invest. 3751, 1944). Explosions and fires may be initiated by discharges of static electricity, sparks from flames, hot surfaces, and spontaneous combustion. Metal powders present a hazard because of their **flammability.** Their combustion is favored during grinding operations in which ball, hammer, or ring-roller mills are employed and during which a high grinding temperature may be reached.

Many finely divided metal powders in suspension in air are potential **explosion hazards,** and causes for ignition of such dust clouds are numerous [Hartmann and Greenwald, *Min. Metall.*, **26,** 331 (1945)]. Concentration of the dust in air and its particle size are important factors that determine explosibility. Below a lower limit of concentration, no explosion can result because the heat of combustion is insufficient to propagate it. Above a maximum limiting concentration, an explosion cannot be produced because insufficient oxygen is available. The finer the particles, the more easily is ignition accomplished and the more rapid is the rate of combustion. This is illustrated in Fig. 20-7.

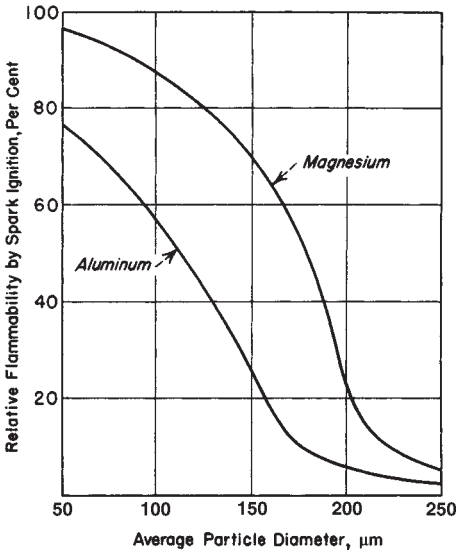


FIG. 20-7 Effect of fineness on the flammability of metal powders. (*Hartmann, Nagy, and Brown, U.S. Bur. Mines Rep. Invest. 3722, 1943.*)

Isolation of the mills, use of nonsparking materials of construction, and magnetic separators to remove foreign magnetic material from the feed are useful **precautions** (Hartman, Nagy, and Brown, U.S. Bur. Mines Rep. Invest. **3722,** 1943). Stainless steel has less sparking tendency than ordinary steel or forgings.

Reduction of the oxygen content of air present in grinding systems is a means for preventing dust explosions in equipment (Brown, U.S. Dep. Agri. Tech. Bull. **74,** 1928). Maintenance of oxygen content below 12 percent should be safe for most materials, but 8 percent is recommended for sulfur grinding. The use of **inert gas** has particular adaptation to pulverizers equipped with air classification; flue gas can be used for this purpose, and it is mixed with the air normally present in a system (see subsection "Chemicals and Soaps" for sulfur grinding). Despite the protection afforded by the use of inert gas, equipment should be provided with explosion vents, and structures should be designed with venting in mind [Brown and Hanson, *Chem. Metall. Eng.*, **40,** 116 (1933)].

Hard rubber presents a fire hazard when reduced on steam-heated rolls (see subsection "Organic Polymers"). Its dust is explosive [Twiss and McGowan, *India Rubber J.*, **107,** 292 (1944)].

An annual publication, *National Fire Codes for the Prevention of Dust Explosions,* is available from the National Fire Protection Association, Quincy, Massachusetts, and should be of interest to those handling hazardous powders.

ATTAINABLE PRODUCT SIZE AND ENERGY REQUIRED

The fineness to which a material is ground has a marked effect on its production rate. Figure 20-8 is an example showing how the capacity decreases and the specific energy and cost increase as the product is ground finer.

Concern about the rising cost of energy has led to publication of a report (National Materials Advisory Board, *Comminution and Energy Consumption,* Publ. NMAB-364, National Academy Press, Washington, 1981; available National Technical Information Service, Springfield, Va. 22151). This has shown that United States industries use approximately 32 billion kWh of electrical energy per annum in size-reduction operations. More than half of this energy is consumed in the crushing and grinding of minerals, one-quarter in the production of cement, one-eighth in coal, and one-eighth in agricultural products. The report recommends that five areas be considered to save energy: classification-device design, mill design, control, additives, and materials to resist wear. It reviews these areas with an extensive bibliography.

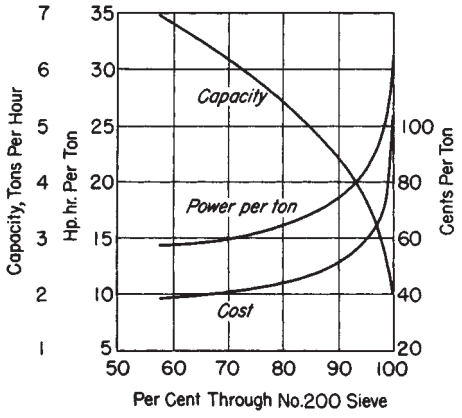


FIG. 20-8 Variation in capacity, power, and cost of grinding relative to fineness of product.

Energy Laws Several laws have been proposed to relate size reduction to a single variable, the energy input to the mill. These laws are encompassed in a general differential equation (Walker, Lewis, McAdams, and Gilliland, *Principles of Chemical Engineering,* 3d ed., McGraw-Hill, New York, 1937):

$$dE = -C\,dX/X^n \tag{20-10}$$

where E is the work done, X is the particle size, and C and n are constants. For $n = 1$ the solution is *Kick's law* (Kick, *Das Gasetz der proportionalen Widerstande und seine Anwendung,* Leipzig, 1885). The law can be written

$$E = C \log (X_F/X_P) \tag{20-11}$$

where X_F is the feed-particle size, X_P is the product size, and X_F/X_P is the reduction ratio. For $n > 1$ the solution is

$$E = \left(\frac{C}{n-1}\right)\left(\frac{1}{X_P^n - 1} - \frac{1}{X_F^n - 1}\right) \tag{20-12}$$

For $n = 2$ this becomes *Rittinger's law,* which states that the energy is proportional to the new surface produced (Rittinger, *Lehrbuch der Aufbereitungskunde,* Ernst and Korn, Berlin, 1867).

The *Bond law* corresponds to the case in which $n = 1.5$ [Bond, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, **193,** 484 (1952)]:

$$E = 100E_i\left(\frac{1}{\sqrt{X_P}} - \frac{1}{\sqrt{X_F}}\right) \tag{20-13}$$

where E_i is the **Bond work index,** or work required to reduce a unit weight from a theoretical infinite size to 80 percent passing 100 μm. Extensive data on the work index have made this law useful for rough mill sizing. Summary data are given in Table 20-4.

The work index may be found experimentally from laboratory crushing and grinding tests or from commercial mill operations. Some rules of thumb for extrapolating the work index to conditions different from those measured are that for dry grinding the index must be increased by a factor of 1.34 over that measured in wet grinding; for open-circuit operations another factor of 1.34 is required over that measured in closed circuit; if the product size X_p is extrapolated below 70 μm, an additional correction factor is $(10.3 + X_p)/1.145X_p$. Also for a jaw or gyratory crusher the work index may be estimated from

$$E_i = 2.59C_s/\rho_s \tag{20-14}$$

where C_s = impact crushing resistance, (ft · lb)/in of thickness required to break; ρ_s = specific gravity; and E_i is expressed in kWh/ton.

None of the energy laws apply well in practice, and they have failed to yield a starting point for further development of understanding of milling. They are mainly of historical interest. Most of the early papers

TABLE 20-4 Average Work Indices for Various Materials*

Material	No. of tests	Specific gravity	Work index†	Material	No. of tests	Specific gravity	Work index†
All materials tested	2088	—	13.81	Taconite	66	3.52	14.87
Andesite	6	2.84	22.13	Kyanite	4	3.23	18.87
Barite	11	4.28	6.24	Lead ore	22	3.44	11.40
Basalt	10	2.89	20.41	Lead-zinc ore	27	3.37	11.35
Bauxite	11	2.38	9.45	Limestone	119	2.69	11.61
Cement clinker	60	3.09	13.49	Limestone for cement	62	2.68	10.18
Cement raw material	87	2.67	10.57	Manganese ore	15	3.74	12.46
Chrome ore	4	4.06	9.60	Magnesite, dead burned	1	5.22	16.80
Clay	9	2.23	7.10	Mica	2	2.89	134.50
Clay, calcined	7	2.32	1.43	Molybdenum	6	2.70	12.97
Coal	10	1.63	11.37	Nickel ore	11	3.32	11.88
Coke	12	1.51	20.70	Oil shale	9	1.76	18.10
Coke, fluid petroleum	2	1.63	38.60	Phosphate fertilizer	3	2.65	13.03
Coke, petroleum	2	1.78	73.80	Phosphate rock	27	2.66	10.13
Copper ore	308	3.02	13.13	Potash ore	8	2.37	8.88
Coral	5	2.70	10.16	Potash salt	3	2.18	8.23
Diorite	6	2.78	19.40	Pumice	4	1.96	11.93
Dolomite	18	2.82	11.31	Pyrite ore	4	3.48	8.90
Emery	4	3.48	58.18	Pyrrhotite ore	3	4.04	9.57
Feldspar	8	2.59	11.67	Quartzite	16	2.71	12.18
Ferrochrome	18	6.75	8.87	Quartz	17	2.64	12.77
Ferromanganese	10	5.91	7.77	Rutile ore	5	2.84	12.12
Ferrosilicon	15	4.91	12.83	Sandstone	8	2.68	11.53
Flint	5	2.65	26.16	Shale	13	2.58	16.40
Fluorspar	8	2.98	9.76	Silica	7	2.71	13.53
Gabbro	4	2.83	18.45	Silica sand	17	2.65	16.46
Galena	7	5.39	10.19	Silicon carbide	7	2.73	26.17
Garnet	3	3.30	12.37	Silver ore	6	2.72	17.30
Glass	5	2.58	3.08	Sinter	9	3.00	8.77
Gneiss	3	2.71	20.13	Slag	12	2.93	15.76
Gold ore	209	2.86	14.83	Slag, iron blast furnace	6	2.39	12.16
Granite	74	2.68	14.39	Slate	5	2.48	13.83
Graphite	6	1.75	45.03	Sodium silicate	3	2.10	13.00
Gravel	42	2.70	25.17	Spodumene ore	7	2.75	13.70
Gypsum rock	5	2.69	8.16	Syenite	3	2.73	14.90
Ilmenite	7	4.27	13.11	Tile	3	2.59	15.53
Iron ore	8	3.96	15.44	Tin ore	9	3.94	10.81
Hematite	79	3.76	12.68	Titanium ore	16	4.23	11.88
Hematite—specular	74	3.29	15.40	Trap rock	49	2.86	21.10
Oolitic	6	3.32	11.33	Uranium ore	20	2.70	17.93
Limanite	2	2.53	8.45	Zinc ore	10	3.68	12.42
Magnetite	83	3.88	10.21				

*Allis-Chalmers Corporation.
†Caution should be used in applying the average work index values listed here to specific installations, since individual variations between materials in any classification may be quite large.

supporting one law or another were based on extrapolations of size distributions to finer sizes on the assumption of one or another size-distribution law. With present particle-size-analysis techniques applicable to the finest sizes, such confusion is no longer necessary. The relation of energy expenditure to the size distribution produced has been thoroughly examined [Arbiter and Bhrany, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **217,** 245–252 (1960); Harris, *Inst. Min. Metall. Trans.,* **75**(3), C37 (1966); Holmes, *Trans. Inst. Chem. Eng.* (*London*), **35,** 125–141 (1957); and Kelleher, *Br. Chem. Eng.,* **4,** 467–477 (1959); **5,** 773–783 (1960)].

Grinding Efficiency The energy efficiency of a grinding operation is defined as the energy consumed compared with some ideal energy requirement.

The theoretical energy efficiency of grinding operations is 0.06 to 1 percent, based on values of the surface energy of quartz [Martin, *Trans. Inst. Chem. Eng.* (*London*), **4,** 42 (1926); Gaudin, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **73,** 253 (1926)]. Uncertainty in these results is due to uncertainty in the theoretical surface energy.

A definitive monograph (Kuznetzov, *Surface Energy of Solids,* English translation, H. M. Stationery Office, London, 1957) established that most laboratory methods of measuring surface energy introduce large errors, but the cleavage method of Obreimov [Gilman, *J. Appl. Phys.,* **31,** 2208 (1960)] gave results for sodium chloride that agree with theoretical lattice calculations. Later studies by Raasch [*Int. J. Frac. Mech.,* **7**(9), 289 (1971)] and by Burns [*Philos. Mag.,* **25**(1), 131 (1972)] conclude that these measurements are valid when 50 percent corrections are added for the bending energy of the crystal. Kuznetzov ranks other materials by a relative wear test. His results substantiate the efficiencies given earlier. Attempts to measure efficiency of the grinding process by calorimetry involve errors that exceed the theoretical surface energy of the material being ground.

Practical energy efficiency is defined as the efficiency of technical grinding compared with that of laboratory crushing experiments. Practical efficiencies of 25 to 60 percent have been shown [Wilson, *Min. Technol.,* Tech. Publ. 810, 1937; and Bond and Maxson, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **134,** 296 (1939)].

An **energy coefficient** is sometimes based on Rittinger's law, i.e., new surface produced per unit of energy input. Usually time of grinding is the experimental variable, which is expressed indirectly as energy. The energy coefficient may also be expressed as tons per horsepower-hour passing a certain size. The value of this coefficient is between about 0.02 and 0.1 for wet ball-mill pulverizing hard to medium-hard minerals to No. 200 sieve size (74 μm).

The curves in Fig. 20-9 show decreasing production rate with increasing **moisture content.** (Occasionally, a small amount of water may be beneficial over complete dryness.) All three materials were being ground to 99.9 percent through a No. 200 sieve.

Fine Size Limit (See also Single-Particle Fracture above.)

It has long been thought that a **limiting size** is attainable. New technologies such as pressed ceramics and Xerox toners require finer sizes,

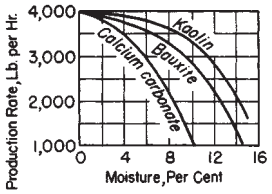


FIG. 20-9 Effect of moisture on the production rate of a pulverizer. [*Work,* Chem. Metall. Eng., ***40,*** *306 (1933).*]

and this again questions the existence of a limit. There are three theories for such a limit. Bradshaw [*J. Chem. Phys.,* **19,** 1057–1059 (1951)] thought that *reagglomeration* is responsible, especially in ball mills. Schönert and Steier [*Chem. Ing. Tech.,* **43**(13), 773 (1971)] suggest two other causes: *plastic deformation* and the difficulty of *stressing* fine particles to their breaking point. The latter stems from the Griffith crack theory, which requires that the particle have enough stored stress energy to allow a crack to propagate. A 10-μm glass particle requires 140 kPa/mm^2 tensile stress. Although both of these mechanisms can be limiting, recent experimental evidence indicates that plastic deformation can increase the resistance of even the most brittle materials on a fine scale. Rumpf and Schönert (*Third European Symposium on Size Reduction,* op. cit., 1972, p. 27) observed plastic deformation in crushing fine glass spheres. Schönert and Steier (loc. cit.) in electron-microscope photographs observed plastic deformation in crushing limestone particles as large as 3 to 4 μm and quartz particles of 2 to 3 μm. This deformation spreads a stress that would otherwise produce brittle fracture. Gane [*Philos. Mag.,* **25**(1), 25 (1972)] observed plastic deformation in magnesium oxide crystals 0.2 to 0.4 μm in size. The strengths average 180 kg/mm^2, which is 15 times the strength of large MgO crystals but one-tenth of the theoretical strength. Further proof is given by Weichert and Schönert [*J. Mech. Phys. Solids,* **22,** 127 (1974)], who analyze and measure the temperature rise at a propagating crack tip. They estimate that irreversible deformation occurs in a zone of radius about 30 A running along at the tip. The energy release causes temperatures as high as 1500 K above ambient temperature at the tip. This temperature explains plastic flow and even emitted light in some cases. Therefore, it is proved that plastic deformation can limit the grinding size attainable. Other means than size reduction must be found if particles much finer than 0.5 μm are wanted.

Dry versus Wet Grinding (See under Ball Mills, and Wear.) In practice it is found that finer size can be achieved by **wet grinding** than by **dry grinding.** In wet grinding by ball mills or vibratory mills with suitable surfactants, product sizes of 0.5 μm are attainable. In dry grinding the size is generally limited by ball coating (Bond and Agthe, *Min. Technol.,* AIME Tech. Publ. 1160, 1940) to about 15 μm. In dry grinding with hammer mills or ring-roller mills the limiting size is about 10 to 20 μm. Jet mills are generally limited to a product mean size of 15 μm, although dense particles can be ground to 5 μm because of the greater ratio of inertia to aerodynamic drag.

Dispersing Agents and Grinding Aids There is no doubt that grinding aids are helpful under some conditions. For example, surfactants make it possible to ball-mill magnesium in kerosine to 0.5-μm size [Fochtman, Bitten, and Katz, *Ind. Eng. Chem. Prod. Res. Dev.,* **2,** 212–216 (1963)]. Without surfactants the size attainable was 3 μm, and of course the rate of grinding was very slow at sizes below this. Also, the water in wet grinding may be considered to act as an additive.

Chemical agents that increase the rate of grinding are an attractive prospect since their cost is low. However, despite a voluminous literature on the subject, there is no accepted scientific method to choose such aids; there is not even agreement on the mechanisms by which they work. The subject has been recently reviewed [Fuerstenau, *KONA Powder and Particle,* **13,** 5–17 (1995)].

In wet grinding there are several theories, which have been reviewed [Somasundaran and Lin, *Ind. Eng. Chem. Process Des. Dev.,* **11**(3), 321 (1972); Snow, annual reviews, op. cit., 1970–1974. See also Rose, *Ball and Tube Milling,* Constable, London, 1958, pp. 245–249]. The *Rehbinder theory* (Rehbinder, Schreiner, and Zhigach, *Hardness Reducers in Rock Drilling,* Moscow Academy of Science, 1944, transl. Council for Scientific and Industrial Research, Melbourne, Australia, 1948).

Additives can alter the rate of wet ball milling by changing the slurry viscosity or by altering the location of particles with respect to the balls. These effects are discussed under "Tumbling Mills." In conclusion, there is still no theoretical way to select the most effective additive. Empirical investigation, guided by the principles discussed earlier, is the only recourse. There are a number of commercially available grinding aids that may be tried. Also, a kit of 450 surfactants that can be used for systematic trials (Model SU-450, Chem Service Inc., West Chester, PA 19380) is available.

Numerous experimental studies lead to the conclusion that dry grinding is limited by ball coating and that additives function by reducing the tendency to coat (Bond and Agthe, op. cit.). Most materials coat if they are ground fine enough, and softer materials coat at larger sizes than hard materials. The presence of more than a few percent of soft gypsum promotes ball coating in cement-clinker grinding. The presence of a considerable amount of coarse particles above 35 mesh inhibits coating. Balls coat more readily as they become scratched. Small amounts of moisture may increase or decrease ball coating, and dry materials also coat.

Materials used as grinding aids include solids such as graphite, oleoresinous liquid materials, volatile solids, and vapors. The complex effects of vapors have been extensively studied [Goette and Ziegler, *Z. Ver. Dtsch. Ing.,* **98,** 373–376 (1956); and Locher and von Seebach, *Ind. Eng. Chem. Process Des. Dev.,* **11**(2), 190 (1972)], but water is the only vapor used in practice.

The most effective additive for dry grinding is fumed silica that has been treated with methyl silazane [Tulis, *J. Hazard. Mater.,* **4,** 3 (1980)].

SIZE REDUCTION COMBINED WITH OTHER OPERATIONS

Practically every solid material undergoes size reduction at some point in its processing cycle. Some of the reasons for size reduction are: (1) to liberate a desired component for subsequent separation, as in separating ores from gangue; (2) to prepare the material for subsequent chemical reaction, i.e., by enlarging the specific surface as in cement manufacture; (3) to subdivide the material so that it can be intimately blended with other components; (4) to meet a size requirement for the quality of the end product, as in fillers or pigments for paints, plastics, agricultural chemicals etc.; (5) to prepare wastes for recycling.

Systems Involving Size Reduction Industrial applications usually involve a number of processing steps combined with size reduction [Hixon, *Chemical Engineering Progress,* **87,** 36–44 (May 1991)]. The most common of these is **size classification.** Often only a particular range of product sizes is wanted for a given application. Since the particle breakage process always yields a spectrum of sizes, the product size can not be directly controlled; however, mill operation can sometimes be varied to produce less fines at the expense of producing more coarse particles. By recycling the classified coarse fraction and regrinding it, production of the wanted size range is optimized. Such an arrangement of classifier and mill is called a **mill circuit,** and is dealt with further below.

More complex systems may include several unit operations such as mixing (Sec. 18), drying (Sec. 12), and agglomerating (see Size Enlargement, this section). Inlet and outlet silencers are helpful to reduce noise from high-speed mills. Chillers, air coolers, and explosion proofing may be added to meet requirements. Weighing and packaging facilities complete the system.

Batch ball mills with low ball charges can be used in dry mixing or standardizing of dyes, pigments, colors, and insecticides to incorporate wetting agents and inert extenders (see also Sec. 21). Disk mills, hammer mills, and other high-speed disintegration equipment are useful for final intensive blending of insecticide compositions, earth colors, cosmetic powders, and a variety of other finely divided materials that tend to agglomerate in ribbon and conical blenders. Liquid sprays or gases may be injected into the mill or air stream, for mixing with the material being pulverized to effect chemical reaction or surface treatment.

The **drying** of materials while they are being pulverized or disintegrated is known variously as "flash" or "dispersion" drying; a generic term is "pneumatic conveying" drying. Data for the grinding and drying of bauxite in a ring-roller mill are given in Table 20-5. A drying system is shown under "Clays and Kaolins," Fig. 20-58.

Milling Problems Materials with low-softening temperatures, such as chocolate, are amenable to pulverizing if proper temperature control is exercised. Compositions containing fats and waxes are pulverized and blended readily if refrigerated air is introduced into their grinding systems (U.S. Patents 1,739,761 and 2,098,798; see also subsection "Organic Polymers" and Hixon loc. cit. for flow sheets). Some materials, such as salt, are very hygroscopic; they pick up water from air and deposit on mill surfaces, forming a hard cake. Mills with air-classification units may be equipped so that the circulating air can be conditioned by mixing with hot or cold air or gases introduced into the mill or by dehumidification to prepare the air for the grinding of hygroscopic materials. Flow sheets including air dryers are also described by Hixon. All organic materials and most metals can form **flammable** or **explosive** mixtures with air (see Safety above). The feed material may be toxic, bioreactive or radioactive, requiring isolation. This may best be accomplished by batch operation. Or the material may be corrosive to mill components. Iron contamination from wear or corrosion of the mill is often a problem. Jet milling is used to produce ultrapure materials for semiconductor manufacture.

Continuous Operation Advantages, which can be very important (Hixon, loc. cit.), are: (1) There is increased economical operation. Less time is needed for start-up and shutdown, and often less maintenance is needed. Because the operating conditions are constant, less operator attention may be needed, and automatic control is more readily applied. (2) It may be more feasible to increase the scale of a continuous system, thus improving unit economy. (3) There is better quality control. This may be the major benefit. Once the operating parameters are properly set, the continuous system will provide a more consistent product. (4) The improvement of the competitive position. A clever arrangement of a system may give an advantage either in product quality or cost. The disadvantages of a continuous system are (1) increased complexity of equipment over batch processing, and (2) the need for more thorough planning, usually requiring pilot-scale testing.

Some special requirements of continuous systems are: (1) Metering the feed. A continuous system must be fed at a precise, uniform rate. (See Sec. 21.) (2) Dust collection. This is a necessary part of most dry-processing systems. Filters are available that can effectively remove dust down to 10 mg/m^3 or less, and operate automatically. (Dust collection is covered in Sec. 17.) (3) On-line analysis. For more precise operation, on-line analysis of product particle size and composition may be desirable. (4) Computer control. Simulation can aid in optimizing system design and computer control.

Beneficiation Ball and pebble mills, batch or continuous, offer considerable opportunity for combining a number of **processing steps** that include grinding [Underwood, *Ind. Eng. Chem.*, **30,** 905 (1938)]. Mills followed by air classifiers can serve to **separate components of mixtures** because of differences in specific gravity and particle size. The removal of impurities by this means is known as **cleaning, concentrating,** or **beneficiating.** Screens are used to separate coarse particles, not easily pulverized, from fine particles of the component that are pulverized readily. Grinding followed by *froth flotation* has become the beneficiation method most widely used for metallic ores and also for nonmetallic minerals such as feldspar. Magnetic separation is the chief means used for upgrading taconite iron ore (see subsection "Ores and Minerals"). Magnetic separators frequently are employed to remove tramp magnetic solids from the feed to high-speed hammer and disk mills.

TABLE 20-5 Operating Data for Grinding and Drying of Bauxite in a Ring-Roller Mill

Initial moisture, %	9.75
Final moisture, %	0.75
Feed, lb./hr	12,560
Product, lb./hr	11,420
Moisture evaporated, lb	1,140
Temperature of gases entering mill, °F	700
Temperature of gases leaving mill, °F	170
Temperature of feed, °F	70
Temperature of material leaving mill, °F	150
Oil consumed, gal	14.3
Heating value of oil, B.t.u./gal	142,000
Thermal efficiency, %	68.5
Total power for drying and pulverizing, hp	105
Power for drying, hp	10
Final product, % through No. 100 sieve	90

Liberation Most ores are heterogeneous, and the objective of grinding is to release the valuable mineral component so that it can be separated. Calculations based on a random-breakage model assuming no preferential breakage [Wiegel and Li, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, **238,** 179–191 (1967)] agreed at least in general trends with plant data on the efficiency of release of mineral grains. Figure 20-10 shows that the desired mineral *B* can be liberated by coarse grinding when the grade is high so that mineral *A* becomes a small fraction and mineral *B* a large fraction of the total volume; mineral *B* can be liberated only by fine grinding below the grain size, when the grade is low so that there is a small proportion of grains of *B*. Similar curves, somewhat displaced in size, resulted from a more detailed integral geometry analysis by Barbery [*Minerals Engineering*, **5**(2), 123–141 (1992)]. There is at present no way to measure grain size on-line, and thus to control liberation. The current status of liberation modeling is given by Mehta et al. [*Powder Technology*, **58**(3), 195–209 (1989)].

Many authors have assumed that breakage occurs preferentially along grain boundaries, but there is scant evidence for this. On the contrary, Gorski [*Bull. Acad. Pol. Sci. Ser. Sci. Tech.*, **20**(12), 929 (1972); CA 79, 20828k], from analysis of microscope sections, finds an intercrystalline character of comminution of dolomite regardless of the type of crusher used.

The liberation of a valuable constituent does not necessarily translate directly into recovery in downstream processes. For example, flotation tends to be more efficient in intermediate sizes than at coarse or fine sizes [McIvor and Finch, *Minerals Engineering*, **4**(1), 9–23 (1991)]. For coarser sizes, failure to liberate may be the limitation; finer sizes that are liberated may still be carried through by the water flow. A conclusion is that overgrinding should be avoided by judicious use of size classifiers with recycle grinding.

Size Reduction Combined with Size Classification Grinding systems are batch or continuous in operation (Fig. 20-11). Most large-scale operations are continuous; batch ball or pebble mills are used

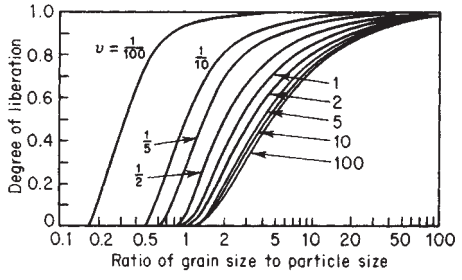


FIG. 20-10 Fraction of mineral *B* that is liberated as a function of volumetric abundance ratio υ of gangue to mineral *B* (1/grade), and ratio of grain size to particle size of broken fragments (1/fineness). [*Wiegel and Li,* Trans. Soc. Min. Eng.-Am. Inst. Min. Metall. Pet. Eng., ***238,*** *179 (1967).*]

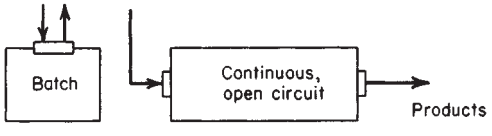


FIG. 20-11 Batch and continuous grinding systems.

only when small quantities are to be processed. Batch operation involves a high labor cost for charging and discharging the mill.

Continuous operation is accomplished in open or closed circuit, as illustrated in Figs. 20-11 and 20-12. **Operating economy** is the object of closed-circuit grinding with size classifiers. The idea is to remove the material from the mill before all of it is ground, separate the fine product in a classifier, and return the coarse for regrinding with the new feed to the mill. A mill with the fines removed in this way performs much more efficiently. Coarse material returned to a mill by a classifier is known as the **circulating load;** its rate may be from 1 to 10 times the production rate. The ability of the mill to transport material may limit the recycle rate; tube mills for use in such circuits may be designed with a smaller length-to-diameter ratio and hence a larger hydraulic gradient for more flow or with compartments separated by diaphragms with lifters.

Internal size classification plays an essential role in the functioning of machines for dry grinding in the fine-size range; particles are retained in the grinding zone until they are as small as required in the finished product; then they are allowed to discharge.

By closed-circuit operation the product size distribution is narrower and will have a larger proportion of particles of the desired size. On the other hand, making a *product size within narrow limits* (such as between 20 and 40 μm) is often requested but usually is not possible regardless of the grinding circuit used. The reason is that particle breakage is a random process, both as to the probability of breakage of particles and as to the sizes of fragments produced from each breakage event. The narrowest size distribution ideally attainable is one that has a slope of 1.0 when plotted on Gates-Gaudin-Schumann coordinates [Eq. (20-2) and Fig. 20-13]. This can be demonstrated by examining the Gaudin-Meloy size distribution [Eq. (20-4)]. This is the distribution produced in a mill when particles are cut into pieces of random size, with r cuts per event. The case in which r is large corresponds to a breakage event producing many fines. The case in which r is 1 corresponds to an ideal case such as a knife cutter, in which each particle is cut once per event and the fragments are removed immediately by the classifier. The Meloy distribution with $r = 1$ reduces to the Schumann distribution with a slope of 1.0. Therefore, no practical grinding operation can have a slope greater than 1.0. Slopes typically range from 0.5 to 0.7. The specified product may still be made, but the finer fraction may have to be disposed of in some way. Within these limits, the size distribution of the classifier product depends both on the recycle ratio and on the sharpness of cut of the classifier used.

Characteristics of Size Classifiers (See Sec. 19: "Screening" on screening equipment and "Wet Classification" on wet classifiers.) Types of classifiers and commercially available equipment are described in the subsection "Particle-Size Classifiers Used with Grinding Mills." The American Institute of Chemical Engineers Equipment Testing Procedures Committee has published a procedure for particle-size classifiers (*Particle-Size Classifiers—A Guide to Performance Evaluation,* 2d ed. American Institute of Chemical Engineers, New York, 1994), including definitions which are followed here.

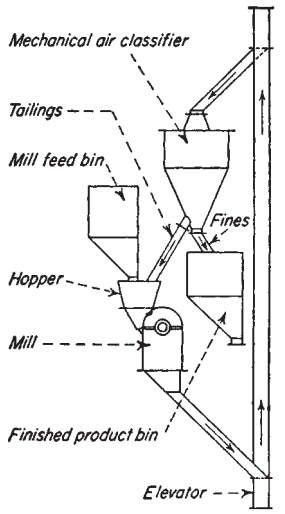


FIG. 20-12 Hammer mill in closed circuit with an air classifier.

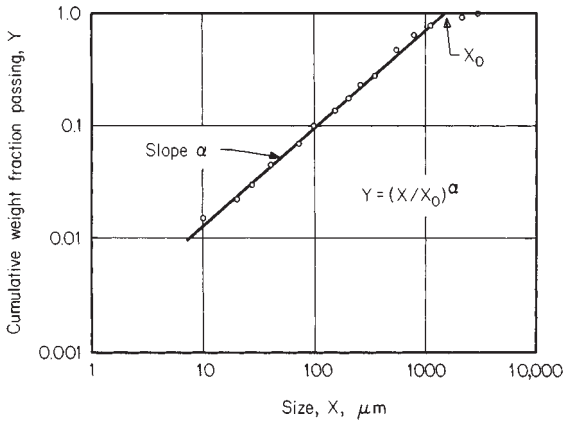


FIG. 20-13 Example of a Gates-Gaudin-Schumann plot of mill-product-size distribution.

Three parameters define the performance of a classifier. These are *cut size, sharpness* of cut, and *capacity.* Cut size, X_{50}, is the size at which 50 percent of the material goes into the coarse product and 50 percent into the fine. (This should not be confused with the "cutoff size," a name sometimes given to the top size of the fine product.)

Size selectivity is the most thorough method of expressing classifier performance under a given set of operating conditions. Cut size and sharpness can be calculated from size-selectivity data. Size selectivity is defined by

$$\eta_X = \frac{\text{quantity of size } X \text{ entering coarse fraction}}{\text{quantity of size } X \text{ in feed}} \qquad (20\text{-}15)$$

An equivalent mathematical expression is, on a *mass* basis,

$$\eta_X = \frac{q_c dY_c}{q_0 dY_0} = \frac{q_c dY_c}{q_c dY_c + q_f dY_f} \qquad (20\text{-}16)$$

where Y_c is the cumulative percent by mass of coarse fraction less than particle size X, Y_f is the cumulative percent by mass of fine fraction less than particle size X, Y_0 is the cumulative percent by mass of feed less than particle size X, q_c is the coarse-fraction mass flow rate, q_f is the fine-fraction mass flow rate, and q_0 is the feed mass flow rate.

For purposes of calculating size selectivity from cumulative particle size distribution data, Eq. (20-16) can be expressed in incremental form as follows:

$$\eta_{X_i} = \frac{q_c \Delta Y_{ci}}{q_c \Delta Y_{ci} + q_f \Delta Y_{fi}} \qquad (20\text{-}17)$$

where ΔY_{ci} and ΔY_{fi} are the cumulative size-distribution intervals of coarse and fine fractions associated with the size interval ΔX_i respectively. An interval representative size X_i is arbitrarily taken as the midpoint of ΔX_i.

See the American Institute of Chemical Engineers classifier test procedure for a sample calculation of classifier selectivity. This example is plotted in Fig. 20-14.

There are many ways in which sharpness can be expressed. One index that has been widely used is the ratio

$$\beta = X_{25}/X_{75} \qquad (20\text{-}18)$$

where β is the sharpness index, X_{75} is the particle size corresponding to the 75 percent classifier selectivity value, and X_{25} is the particle size corresponding to the 25 percent value. For perfect classification, β has a value of unit; the smaller β, the poorer the sharpness of classification.

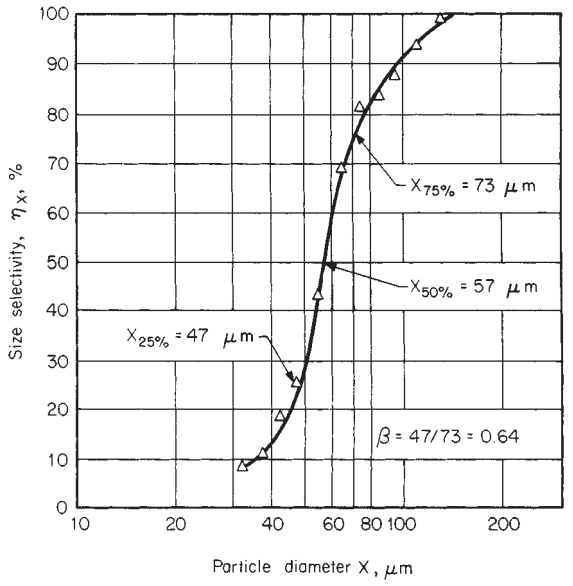


FIG. 20-14 Size-selectivity example.

Several empirical formulas for classifier selectivity have been proposed. Such a formula is needed for computer simulation of mill circuits. The following formula has been found to fit data from several field installations for classifiers of many types, including vibrating screens (Vaillant, AIME Tech. Pap. 67B26, 1967).

$$C_x = 1 - (1 - a)\exp b\left(1 - \frac{X}{X_0}\right) \qquad \text{for } X > X_0$$
$$= a \qquad \text{for } X \leqq X_0 \qquad (20\text{-}19)$$

where a, b, and X_0 are constants and X is the particle size. The agreement is especially good for wet classifying systems. For wet cyclones the factor a and Y_{50} are related to the ratio of overflow to underflow rates [Draper and Lynch, *Proc. Australas. Inst. Min. Metall.,* **209,** 109 (1964); Mizrahi and Cohen, *Trans. Inst. Min. Metall.,* C318–329 (December 1966); and Lynch and Rao, *Indian J. Tech.,* **6,** 106–114 (April 1968)]. An equation developed by stochastic reasoning for cyclones involves a similar exponential form [Molerus, *Chem. Ing. Tech.,* **39**(13), 792–796 (1967)].

It has been suggested that the circulating load can be calculated by a material balance from size analyses of the feed, fine product, and coarse product of the classifier in a closed-circuit grinding system [Bond, *Rock Prod.,* **41,** 64 (January 1938)]. However, since size analyses are subject to error, it is better to use this information to check the size analyses (Vaillant, op. cit.). The appropriate equation is (Dahl, *Classifier Test Manual,* Portland Cem. Assoc. Bull. MRB-53, 1954)

$$\frac{q_R}{q_R + q_P} = R = \frac{Y_L(X) - Y_P(X)}{Y_R(X) - Y_P(X)} = \text{a constant for all } X \qquad (20\text{-}20)$$

where q_R is tailings, q_P is classifier product, L is mill discharge, R is recycle, and Y is either the fraction of particles in a stream between two sieve sizes or the cumulative fraction retained or passing a sieve of size X.

SIMULATION OF MILLING CIRCUITS

The energy laws of Bond, Kick, and Rittinger relate to grinding from some average feed size to some product size but do not take into account the behavior of different sizes of particles in the mill. Computer simulation, based on population-balance models [Bass, Z. *Angew. Math. Phys.,* **5**(4), 283 (1954)], traces the breakage of each size of particle as a function of grinding time. Furthermore, the simulation models separate the breakage process into two aspects: a breakage rate and a mean fragment-size distribution. These are both functions of the size of particle being broken. They usually are not derived from knowledge of the physics of fracture but are empirical functions fitted to milling data. The following formulation is given in terms of a discrete representation of size distribution; there are comparable equations in integrodifferential form.

Batch Grinding Let w_k = the weight fraction of material retained on each screen of a nest of n screens; w_k is related to P_k, the fraction coarser than size X_k, by

$$w_k = (\partial P_k/\partial X_k)\,\Delta X_k \qquad (20\text{-}21)$$

where ΔX_k is the difference between the openings of screens k and $k + 1$. The **grinding-rate function** S_u is the rate at which the material of upper size u is selected for breakage in an increment of time, relative to the amount of that size present:

$$dw_u/dt = -S_u w_u \qquad (20\text{-}22)$$

The **breakage function** $\Delta B_{k,u}$ gives the size distribution of product breakage of size u into all smaller sizes k. Since some fragments from size u are large enough to remain in the range of size u, the term $\Delta B_{u,u}$ is not zero, and

$$\sum_{k=n}^{u} \Delta B_{k,u} = 1 \qquad (20\text{-}23)$$

The differential equation of batch grinding is deduced from a balance on the material in the size range k. The rate of accumulation of material of size k equals the rate of production from all larger sizes minus the rate of breakage of material of size k:

$$\frac{dw_k}{dt} = \sum_{u=1}^{k} [w_u S_u(t)\,\Delta B_{k,u}] - S_k(t) w_k \qquad (20\text{-}24)$$

In general, S_u is a function of all the milling variables. $\Delta B_{k,u}$ is also a function of breakage conditions. If it is assumed that these functions are constant, then relatively simple solutions of the grinding equation are possible, including an analytical solution [Reid, *Chem. Eng. Sci.,* **20**(11), 953–963 (1965)] and matrix solutions [Broadbent and Callcott, *J. Inst. Fuel,* **29,** 524–539 (1956); **30,** 18–25 (1967); and Meloy and Bergstrom, *7th Int. Min. Proc. Congr. Tech. Pap.,* 1964, pp. 19–31].

Solution of Batch-Mill Equations In general, the grinding equation can be solved by numerical methods—for example, the Euler technique (Austin and Gardner, *1st European Symposium on Size Reduction,* 1962) or the Runge-Kutta technique. The matrix method is a particularly convenient formulation of the Euler technique.

Reid's **analytical solution** is useful for calculating the product as a function of time t for a constant feed composition. It is

$$w_{L,k} = \sum_{n=1}^{k} a_{k,n} \exp(-\bar{S}_n\,\Delta t) \qquad (20\text{-}25)$$

where the subscript L refers to the discharge of the mill, zero to the entrance, and $\bar{S}_n = 1$ "corrected" rate function defined by $\bar{S}_n = (1 - \Delta B_{n,n})$ and B is then normalized with $\Delta B_{n,n} = 0$. The coefficients are

$$a_{k,k} = w_{0k} - \sum_{n=1}^{k-1} a_{k,n} \qquad (20\text{-}26)$$

and

$$a_{k,n} = \sum_{u=n}^{k-1} \frac{S_u\,\Delta B_{k,u} a_{n,u}}{\bar{S}_k - \bar{S}_n} \qquad (20\text{-}27)$$

The coefficients are evaluated in order since they depend on the coefficients already obtained for larger sizes.

The basic idea behind the **Euler method** is to set the change in w per increment of time as

$$\Delta w_k = (dw_k/dt)\,\Delta t \qquad (20\text{-}28)$$

where the derivative is evaluated from Eq. (20-24). Equation (20-28) is applied repeatedly for a succession of small time intervals until the desired duration of milling is reached.

In the matrix method a modified rate function is defined, $S'_k = S_k\,\Delta t$ as the amount of grinding that occurs in some small time Δt. The result is

$$\mathbf{w}_L = (\mathbf{I} + \mathbf{S'B} - \mathbf{S'})\mathbf{w}_F = \mathbf{M}\mathbf{w}_F \qquad (20\text{-}29)$$

where the quantities **w** are vectors, **S′** and **B** are the matrices of rate and breakage functions, and **I** is the unit matrix. This follows because the result obtained by multiplying these matrices is just the sum of products obtained from the Euler method. Equation (20-29) has a physical meaning. The unit matrix times $\mathbf{w}_F$ is simply the amount of feed that is not broken. $\mathbf{S'Bw}_F$ is the amount of feed that is selected and broken into the vector of products. $\mathbf{S'w}_F$ is the amount of material that is broken out of its size range and hence must be subtracted from this element of the product. The entire term in parentheses can be considered as a mill matrix **M.** Thus the milling operation transforms the feed vector into the product vector. Meloy and Bergstrom (op. cit.) pointed out that when Eq. (20-29) is applied over a series of p short-time intervals, the result is

$$\mathbf{w}_L = \mathbf{M}^p \mathbf{w}_F \tag{20-30}$$

Matrix multiplication happens to be cummutative in this special case. It is easy to raise a matrix to a power on a computer since three multiplications give the eighth power, etc. Therefore the matrix formulation is well adapted to computer use.

Continuous-Mill Simulation Batch-grinding experiments are the simplest type of experiments to produce data on grinding coefficients. But scale-up from batch to continuous mills must take into account the **residence-time distribution** in a continuous mill. This distribution is apparent if a tracer experiment is carried out. For this purpose background ore is fed continuously, and a pulse of tagged feed is introduced at time t_0. This tagged material appears in the effluent distributed over a period of time, as shown by a typical curve in Fig. 20-15. Because of this distribution some portions are exposed to grinding for longer times than others. Levenspiel (*Chemical Reaction Engineering,* Wiley, New York, 1962) shows several types of residence-time distribution that can be observed. Data on large mills indicate that a curve like that of Fig. 20-15 is typical (Keienberg et al., *3d European Symposium on Size Reduction,* op. cit., 1972, p. 629). This curve can be accurately expressed as a series of arbitrary functions (Merz and Molerus, *3d European Symposium on Size Reduction,* op. cit., 1972, p. 607). A good fit is more easily obtained if we choose a function that has the right shape since then only the first two moments are needed. The log-normal probability curve fits most available mill data, as was demonstrated by Mori [*Chem. Eng.* (*Japan*), **2**(2), 173 (1964)]. Two examples are shown in Fig. 20-16. The log-normal plot fails only when the mill acts nearly as a perfect mixer.

To measure a residence-time distribution, a pulse of tagged feed is inserted into a continuous mill and the effluent is sampled on a schedule. If it is a dry mill, a soluble tracer such as salt or dye may be used and the samples analyzed conductimetrically or colorimetrically. If it is a wet mill, the tracer must be a solid of similar density to the ore. Materials like copper concentrate, chrome brick, or barites have been used as tracers and analyzed by X-ray fluorescence. To plot results in log-normal coordinates, the concentration data must first be normalized from the form of Fig. 20-15 to the form of cumulative percent discharged, as in Fig. 20-16. For this, one must either know the total amount of pulse fed or determine it by a simple numerical integration

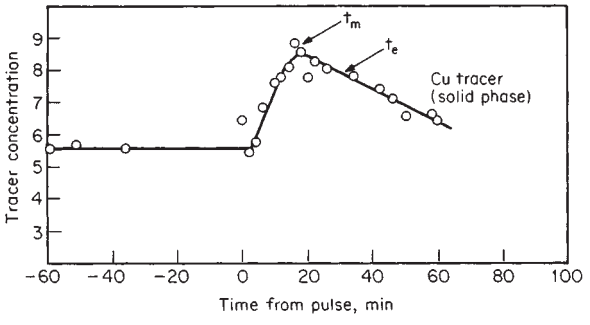
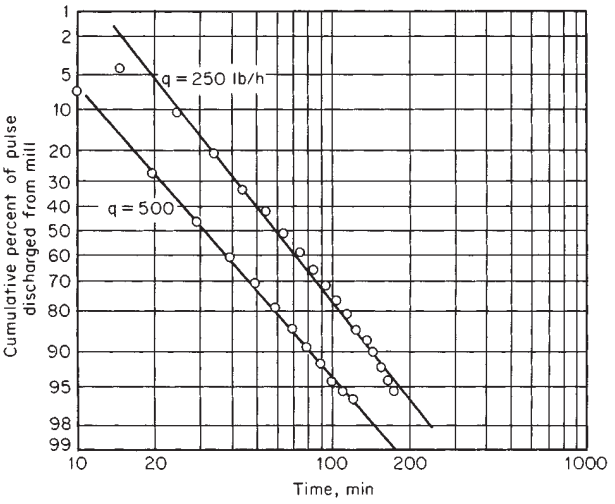


FIG. 20-15 Ore transit through a ball mill. Feed rate is 500 lb h. (*Courtesy Phelps Dodge Corporation.*)



q, lb/h	σ	t_e, min	Dt_e/L^2
250	0.29	39	0.23
500	0.32	18	0.28

FIG. 20-16 Log-normal plot of residence-time distribution in Phelps Dodge mill.

by using a computer. The data are then plotted as in Fig. 20-16, and the coefficients in the log-normal formula of Mori can be read directly from the graph. Here $t_e = t_{50}$ is the time when 50 percent of the pulse has emerged. The standard deviation σ is the time between t_{16} and t_{50} or between t_{50} and t_{84}. Knowing t_e and σ, one can reconstruct the straight line in log-normal coordinates. One can also calculate the vessel dispersion number, Dt_e/L^2, which is a measure of the sharpness of the pulse (Levenspiel, *Chemical Reactor Omnibook,* p. 100.6, Oregon State University Bookstores Inc., 1979. This number has erroneously been called by some the Peclet number). Here D is the particle diffusivity. A few available data are summarized [Snow, *International Conference on Particle Technology,* IIT Research Institute, Chicago, Ill. 60616, 1973, p. 28) for wet mills. Other experiments are presented for dry mills [Hogg et al., *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **258,** 194 (1975)]. The most important variables affecting the vessel dispersion number are L/diameter of the mill, ball size, mill speed, scale expressed either as diameter or as throughput, degree of ball filling, and degree of material filling.

Solution for Continuous Mill In the method of Mori (op. cit.) the residence-time distribution is broken up into a number of segments, and the batch-grinding equation is applied to each of them. The resulting size distribution at the mill discharge is

$$\mathbf{w}(L) = \mathbf{w}(t)\,\Delta\varphi \tag{20-31}$$

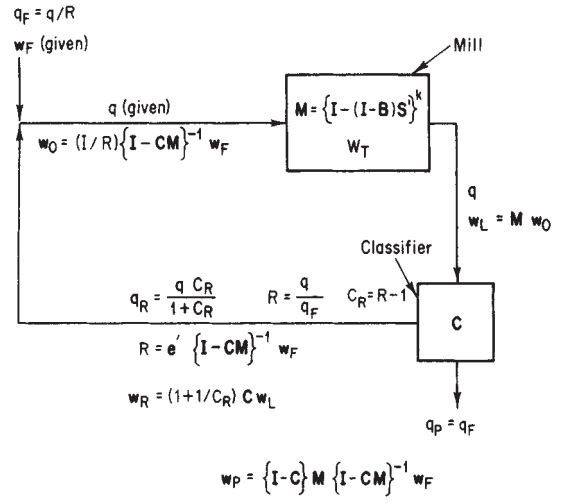
where $\mathbf{w}(t)$ is a matrix of solutions of the batch equation for the series of times t, with corresponding segments of the cumulative residence-time curve.

Using the Reid solution, Eq. (20-25), this becomes

$$\mathbf{w}(L) = \mathbf{RZ}\,\Delta\varphi \tag{20-32}$$

since the Reid solution [Eq. (20-25)] can be separated into a matrix **Z** of exponentials $\exp(-\bar{S}t)$ and another factor R involving only particle sizes. Austin, Klimpel, and Luckie [*Process Engineering of Size Reduction: Ball Milling,* Society of Mining Engineers of AIME, (1984)] incorporated into this form a tanks-in-series model for the residence time distribution.

Closed-Circuit Milling In closed-circuit milling the tailings from a classifier are mixed with fresh feed and recycled to the mill. Calculations can be based on a material balance and an explicit solu-



Nomenclature

C_R = circulating load, $R-1$
C = classifier selectivity matrix, which has classifier selectivity-function values η on diagonal zeros elsewhere
I = identity matrix, which has ones on diagonal, zeros elsewhere
M = mill matrix, which transforms mill-feed-size distribution into mill-product-size distribution
q = flow rate of a material stream
R = recycle ratio q/q_F
w = vector of differential size distribution of a material stream
W_T = holdup, total mass of material in mill

Subscripts:
0 = inlet to mill
F = feed stream
L = mill-discharge stream
P = product stream
R = recycle stream, classifier tailings

FIG. 20-17 Normal closed-circuit continuous grinding system with stream flows and composition matrices, obtained by solving material-balance equations. [*Callcott,* Trans. Inst. Min. Metall., ***76****(1), C1-11 (1967).*]

tion such as Eq. (20-30). Material balances for the normal circuit arrangement (Fig. 20-17) give

$$q = q_F + q_R \tag{20-33}$$

where q = total mill throughput, q_F = rate of feed of new material, and q_R = recycle rate. A material balance on each size gives

$$w_{0,k} = \frac{q_F w_{Fk} + \frac{q_R}{R}\eta_k w_{L,k}}{q} \tag{20-34}$$

where $w_{0,k}$ = fraction of size k in the mixed feed streams, R = the recycle ratio, and η_k = classifier selectivity for size k. With these conditions a calculation of the transient behavior of the mill can be performed by using any method of solving the milling equation and iterating over intervals of time τ = residence time in the mill. This information is important for evaluating mill-circuit-control stability and strategies. If the throughput q is controlled to be a constant, as is often the case, then τ is constant, and a closed-form matrix solution can be found for the steady state [Callcott, *Trans. Inst. Min. Metall.,* **76**(1), C1-11 (1967)]. The resulting flow rates and composition vectors are given in Fig. 20-17. Equations for the reverse-circuit case, in which the feed is classified before it enters the mill, are given by Calcott (loc. cit.). These results can be used to investigate the effects of changes in feed composition on the product. Separate calculations can be made to find the effects of classifier selectivity, mill throughput or recycle, and grindability (rate function) to determine optimum mill-classifier combinations [Lynch, Whiten, and Draper, *Trans. Inst. Min. Metall.,* **76,** C169, 179 (1967)]. Equations such as these form the basis for computer codes that are available for modeling mill circuits [Austin, Klimpel, and Luckie (loc. cit.)].

Data on Behavior of Grinding Functions Although several breakage functions were early suggested [Gardner and Austin, *1st European Symposium on Size Reduction,* op. cit., 1962, p. 217; Broadbent and Calcott, *J. Inst. Fuel,* **29,** 524 (1956); 528 (1956); 18 (1957); **30,** 21 (1957)], the simple Gates-Gaudin-Schumann equation [Eq. (20-2) and Fig. 20-13] has been most widely used to fit ball-mill data. For example, this form was assumed by Herbst and Fuerstenau [*Trans. Am. Inst. Min. Metall. Pet. Eng.,* **241**(4), 538 (1968)] and Kelsall et al. [*Powder Technol.,* **1**(5), 291 (1968); **2**(3), 162 (1968); **3**(3), 170 (1970)]. More recently it has been observed that when the Schumann equation is used, the amount of coarse fragments cannot be made to agree with the mill-product distribution regardless of the choice of rate function. This points to the need for a breakage function that has more coarse fragments, such as the function used by Reid and Stewart (Chemica meeting, 1970) and Stewart and Restarick [*Proc. Australas. Inst. Min. Metall.,* **239,** 81 (1971)] and shown in Fig. 20-18. This graph can be fitted by a *double Schumann equation*

$$B(X) = A\left(\frac{X}{X_0}\right)^s + (1-A)\left(\frac{X}{X_0}\right)^r \tag{20-35}$$

where A is a coefficient less than 1.

In the investigations mentioned earlier the breakage function was assumed to be normalizable; i.e., the shape was independent of X_0. Austin and Luckie [*Powder Technol.,* **5**(5), 267 (1972)] allowed the coefficient A to vary with the size of particle breaking when grinding soft feeds.

Grinding-Rate Functions These were determined by tracer experiments in laboratory mills by Kelsall et al. (op. cit.) as shown in Fig. 20-19 and in similar work by Szantho and Fuhrmann [*Aufbereit. Tech.,* **9**(5), 222 (1968)]. These curves can be fitted by the following equation:

$$\frac{S}{S_{\max}} = \left(\frac{X}{X_{\max}}\right)^{\alpha} \exp\left(-\frac{X}{X_{\max}}\right) \tag{20-36}$$

That a maximum must exist should be apparent from the observation of Coghill and Devaney (U.S. Bur. Mines Tech. Pap., 1937, p. 581) that there is an optimum ball size for each feed size. Figure 20-19

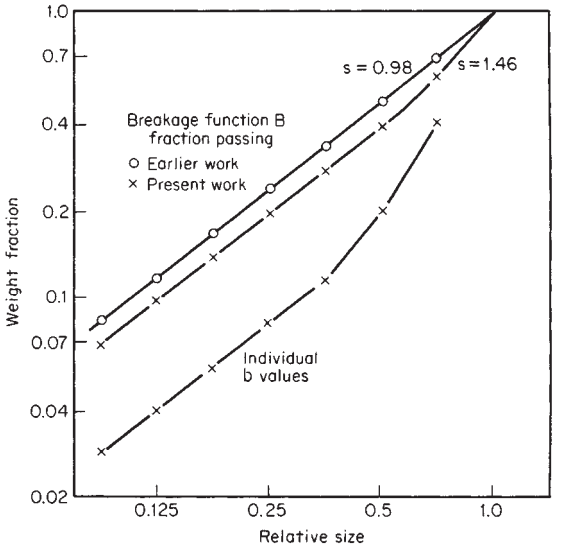


FIG. 20-18 Experimental breakage functions. (*Reid and Stewart, Chemica meeting, 1970.*)

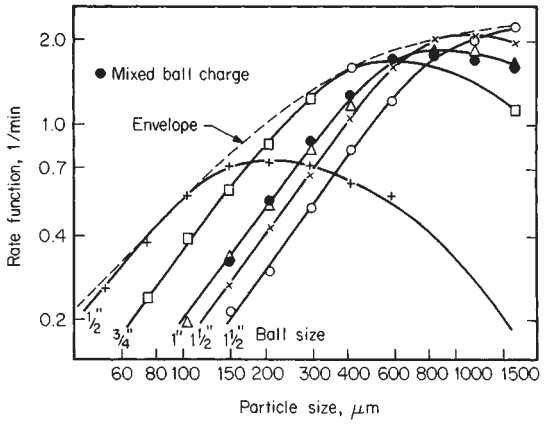


FIG. 20-19 Variation of rate function with size of feed particles and size of balls in a ball mill. [*Kelsall, Reid, and Restarick,* Powder Technol., ***1****(5), 291 (1968).*]

shows that the position of this maximum depends on the ball size. In fact, the feed size for which S is a maximum can be estimated by inverting the formula for optimum ball size given by Coghill and Devaney under "Tumbling Mills."

Scale-Up Based on Energy Since large mills are usually sized on the basis of power draft (see subsection "Energy Laws"), it is appropriate to scale up or convert from batch to continuous data by

$$S(X)_{\text{cont}} = S(X)_{\text{batch}} \frac{(W_T/KW)_{\text{batch}}}{(W_T/KW)_{\text{cont}}} \qquad (20\text{-}37)$$

W_T is usually not known for continuous mills, but it can be determined from $W_T = t_e Q$, where t_e is determined by a tracer measurement. Eq. (20-37) will be valid if the holdup W_T is geometrically similar in the two mills or if operating conditions are in the range in which total production is independent of holdup. From studies of the kinetics of milling [Patat and Mempel, *Chem. Ing. Tech.*, **37**(9), 933; (11), 1146; (12), 1259 (1965)] there is a range of holdup in which this is true. More generally, Austin, Luckie, and Klimpel (loc. cit.) developed empirical relations to predict S as holdup varies. In particular, they observe a slowing of grinding rate when mill filling exceeds ball void volume due to cushioning.

Parameters for Scale-Up Before simulation equations can be used, the parameter matrices **S** and **B** must be back-calculated from experimental data, which turns out to be difficult. One reason is that **S** and **B** occur as a product, so they are to some extent indeterminate; errors in one tend to be compensated by the other. Also, the number of parameters is larger than the number of data values from a single size-distribution measurement; but this is overcome by using data from grinding tests at a series of grinding times. This should be done anyway, since the empirical parameters should be determined to be valid over the experimental range of grinding times.

It may be easier to fit the parameters by forcing them to follow specified functional forms. In earliest attempts it was assumed that the forms should be normalizable (have the same shape whatever the size being broken). With complex ores containing minerals of different friability, the grinding functions **S** and **B** exhibit complex behavior near the grain size (Choi et al., *Particulate and Multiphase Processes Conference Proceedings,* **1,** 903–916.) **B** is not normalizable with respect to feed size and **S** does not follow a simple power law.

There are also experimental problems: When a feed size distribution is ground for a short time, there is not enough change in the size distribution in the mill to distinguish between particles being broken into and out of intermediate sizes, unless individual feed-size ranges are tagged. Feeding narrow-size fractions alone solves the problem, but changes the milling environment; the presence of fines affects the grinding of coarser sizes. Gupta et al. [*Powder Technology,* **28**(1), 97–106 (1981)] ground narrow fractions separately, but subtracted out the effect of the first 3 min of grinding, after which the behavior had become steady. Another experimental difficulty arises from the recycle of fines in a closed circuit, which soon "contaminates" the size distribution in the mill; it is better to conduct experiments in open circuit, or in batch mills on a laboratory scale.

There are few data demonstrating scale-up of the grinding-rate functions **S** and **B** from pilot- to industrial-scale mills. Weller et al. [*International J. Mineral Processing,* **22,** 119–147 (1988)] ground chalcopyrite ore in pilot and plant mills and compared predicted parameters with laboratory data of Kelsall [*Electrical Engineering Transactions,* Institution of Engineers Australia, **EE5**(1), 155–169 (1969)] and Austin Klimpel & Luckie (*Process Engineering of Size Reduction, Ball Milling,* Society of Mining Engineers, NY, 1984) for quartz. **S** has a maximum for a particle size that depends on ball size according to Fig. 20-19, which can be expressed as

$$X_s/X_t = (d_s/d_t)^{2.4}$$

where s = scaled-up mill, t = test mill, d = ball size, X = particle size of maximum rate. Changing ball size also changes the rates according to $\mathbf{S}_s/\mathbf{S}_t = (d_s/d_t)^{0.55}$. These relations shift one rate curve onto another and allow scale-up to a different ball size. Mill diameter also affects rate by a factor $(D_s/D_t)^{0.5}$. Lynch [*Mineral crushing and grinding circuits, their simulation optimization design and control,* Elsevier Scientific Publishing Co., Amsterdam, New York (1977)], and Austin, Klimpel, and Luckie (loc. cit.) developed scale-up factors for ball load, mill filling, and mill speed. In addition, slurry solids content is known to affect the rate, through its effect on slurry rheology. Austin, Klimpel, and Luckie (loc. cit.) present more complete simulation examples and compare them with experimental data to study scale-up and optimization of open and closed circuits, including classifiers such as hydrocyclones and screen bends. Differences in the classifier will affect the rates in a closed circuit. For these reasons scale-up is likely to be uncertain unless conditions in the large mill are as close as possible to those in the test mill.

Control of Grinding Circuits Mineral processing plants require constant supervision and intervention by operators or controllers. Conditions such as feed hardness, grade, grain size, etc., change substantially as ore is delivered from different locations in the mine. Typically the objective of control is to maximize the production of the valuable component per unit time, or to maximize throughput while maintaining a constant grind size. Also, it is necessary to control individual process units so that they run smoothly and in harmony.

Measuring process parameters on full-scale plants is notoriously difficult, but is needed for control. Usually few of the important variables are accessible to measurement. Recycle of material makes it difficult to isolate the effects of changes to individual process units in the circuit. Newer plants have more instrumentation, including on-line viscosimeters [Kawatra and Eisele, *International J. Mineral Processing,* **22,** 251–259 (1988)], mineral composition by on-line X-ray fluorescence, belt feeder weighers, etc., but the information is always incomplete. Therefore it is helpful to have models to predict quantities that cannot be measured while measuring those that can.

Some plants have been using computer control for 20 years. Control systems in industrial use typically consist of individual feedback and feedforward loops. Horst and Enochs [*Engineering & Mining J.,* **181**(6), 69–171 (1980)] reported that installation of single-variable automatic controls improved performance of 20 mineral processing plants by 2 to 10 percent. But interactions among the processes make it difficult for independent controllers to control the circuit optimally.

Optimal control refers first to controlling the circuit dynamically so that it operates close to its optimum state. The *state* is the combination of variables that define the operation of the circuit. The optimum state varies as conditions change. Second, optimal control refers to a mathematical process to find an optimum path to move from a given state to the optimum state, based on minimizing an objective function [as used in control theory [Herbst et al., *International J. Mineral Processing,* **22,** 275–296 (1988)]. Other mathematical approaches have been published as well (Hulbert et al., Automation in Mining, Mineral and Metal Processing: Proceedings of 3rd IFAC Symposium, 311–322, 1980; Romberg, First IFAC Symposium on Automation for Mineral Resource Development, 289, 1985)].

The difficulty with individual PID (proportional-integral-differential) controllers is that each controller only manipulates one variable to achieve a desired effect, whereas the grinding circuit is *multivariate.* For example [Rajamani and Herbst, *Chem. Engr. Science,* **46**(3), 861–879 (1991)], to control the fineness of a ball-mill circuit one can vary either the ore-feed rate to the circuit or the water addition to the sump. Adding water dilutes the slurry going to the hydrocyclone, causing it to separate at a finer size. But then the cyclone sends more recycle back to the mill, loading it more and resulting in a coarser grind. If instead one controls the feed rate, the mill grinds finer, and indirectly the cyclone separates out more fines. Thus, both ore-feed rate and water addition influence more than one variable. As a result PID controllers cause the output to oscillate, as Rajamani and Herbst showed experimentally. The circuit tends to be unstable, and long time delays exist (Metzner and MacLeod, 7th IFAC Symposium on Intelligent Tuning and Adaptive Control, 163–169, 1991). Another difficulty with PID controllers is that their tuning changes depending on the operating conditions. They can be tuned for a rapid response when the ore is soft, but when it is harder the response is more sensitive and the gains have to be reduced to prevent overshoot.

Developing a multivariate control model is difficult because the process is complex. One approach is simplification; meaningful control results can be obtained with as few as two particle sizes in the model (Rajamani and Herbst, loc. cit.). Another approach is to use more powerful inexpensive computers. Complex calculations that previously seemed only of academic interest are now or will soon become practical to perform on-line. The mathematical complexity is also an impediment to understanding, but the commercial availability of packaged software for on-line control will overcome this problem. Software packages that enable grinding-circuit analysis, scale-up design, and flow-sheet optimization have been developed and are widely applied (Herbst et al., *MODSIM User's Manual,* Univ of Utah, Salt Lake City, 1986; Herbst et al., *ESTIMILL User's Manual,* Univ of Utah, Salt Lake City, 1977; King, *MODSIM, Report No. 9,* Dept. of Metallurgy, Univ. Witwatersrand, Johannesburg, 1983; Jamsa, Acta Polytechnica Scandinavica, *Mathematics and Computer Science Series No. 57,* 32 pp., 1990).

Herbst et al. [*International J. Mineral Processing,* **22,** 273–296 (1988)] describe the software modules in an optimum controller for a grinding circuit. The *process model* can be an empirical model as some authors have used. A phenomenological model can give more accurate predictions, and can be extrapolated, for example from pilot- to full-scale application, if scale-up rules are known. Normally the model is a variant of the population balance equations given in the previous section.

Rajamani and Herbst (loc. cit.) compared control of an experimental pilot-mill circuit using feedback and optimal control. Feedback control resulted in oscillatory behavior. Optimal control settled rapidly to the final value, although there was more noise in the results. A more complete model should give even better results.

If individual controllers are used instead of optimal computer control, several strategies are possible. In one strategy (Lynch and Elber, *3rd IFAC Symposium on Automation of Mining, Mineral and Metal Processing,* 25–32, 1980) the slurry-pump rate is controlled to maintain sump-level constant, which results in smooth cyclone operation. The water-feed rate is ratioed to the ore-feed rate, which keeps the circulating load from oscillating. The ore-feed rate is then controlled to maintain product-particle size.

Improved instrumentation can improve control by measuring more directly the variables governing the internal behavior of the mill. By installing an electrical conductivity probe in the wall of the mill, Moys and Montini [*CIM Bulletin,* **80**(907), 52–6 (1987)] were able to detect the position of the ball mass during dynamic operation. This together with on-line measurement of slurry viscosity (see rheological properties, p. 20–32d) made it possible to control the mill at the desired operating point.

CRUSHING AND GRINDING EQUIPMENT

CLASSIFICATION AND SELECTION OF EQUIPMENT

A wide variety of size-reduction equipment is available. The chief reasons for lack of standardization are the variety of products to be ground and product qualities demanded, the limited amount of useful grinding theory, and the requirements by different industries in the economic balance between investment cost and operating cost. Some differences exist for the sake of difference; sometimes similarities are advertised as differences [Rumpf, *Chem. Ing. Tech.,* **37**(3), 187–202 (1965)].

Equipment may be classified according to the way in which forces are applied, as follows (Rumpf, loc. cit.):

1. Between two solid surfaces (Fig. 20-20*a,* crushing or attrition; Fig. 20-20*b,* shearing; Fig. 20-20*c,* crushing in a particle bed)
2. Impact at one solid surface (Fig. 20-20*d*), or between particles (Fig. 20-20*e*)
3. By shear action of the surrounding medium (Fig. 20-20*f,* colloid mill)
4. Nonmechanical introduction of energy (Thermal shock, explosive shattering, electrohydraulic)

A practical **classification of crushing and grinding equipment** is given in Table 20-6.

A guide to the *selection* of equipment may be based on feed *size* and *hardness* (see subsection "Grindability") as shown in Table 20-7. It should be emphasized that Table 20-7 is merely a guide and that exceptions can be found in practice.

A number of general principles govern the **selection of crushers** [Riley, *Chem. Process Eng.* (January 1953)]. When the rock contains a predominant amount of material that has a tendency to be cohesive when moist, such as clay, any form of repeated pressure crusher will show a tendency for the fines to pack in the outlet of the crushing zone and prevent free discharge at fine settings. Impact breakers are then suitable, provided that the rock is not harder and more abrasive than limestone with 5 percent silica.

When the rock is not hard but cohesive, toothed rolls give satisfactory performance. With harder rocks, jaw and gyratory crushers are required, and the jaw crusher is less prone to clogging than the gyratory. In crushing throughputs of a few hundred tons per hour, a jaw or impact crusher may be satisfactory, but for the largest capacities the gyratory is unsurpassed. For secondary crushing the high-speed conical-head gyratory is unsurpassed except when sticky material precludes its use. For very hard ores a rod mill may compete effectively. If a wide size distribution is to be avoided, a compression-type crusher is best; if the product requires fragments of compact shape,

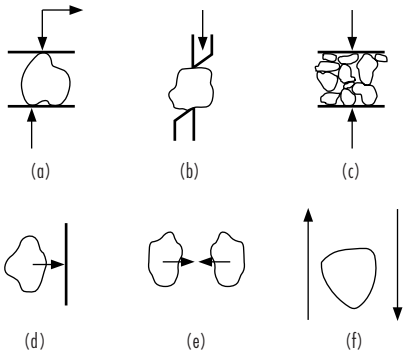


FIG. 20-20 Stressing mechanisms to cause size reduction. [*Rumpf,* Chem. Eng. Tech., *37(3), 187–202 (1965).*]

TABLE 20-6 Types of Size-Reduction Equipment

- *A.* Jaw crushers:
  - 1. Blake
  - 2. Overhead eccentric
- *B.* Gyratory crushers:
  - 1. Primary
  - 2. Secondary
  - 3. Cone
- *C.* Heavy-duty impact mills:
  - 1. Rotor breakers
  - 2. Hammer mills
  - 3. Cage impactors
- *D.* Roll crushers:
  - 1. Smooth rolls (double)
  - 2. Toothed rolls (single and double)
  - 3. Roll press
- *E.* Dry pans and chaser mills
- *F.* Shredders:
  - 1. Toothed shredders
  - 2. Cage disintegrators
  - 3. Disk mills
- *G.* Rotary cutters and dicers
- *H.* Media mills:
  - 1. Ball, pebble, rod, and compartment mills:
    - *a.* Batch
    - *b.* Continuous
  - 2. Autogenous tumbling mills
  - 3. Stirred ball and bead mills
  - 4. Vibratory mills
- *I.* Medium peripheral-speed mills:
  - 1. Ring-roll and bowl mills
  - 2. Roll mills, cereal type
  - 3. Roll mills, paint and rubber types
  - 4. Buhrstones
- *J.* High-peripheral-speed mills:
  - 1. Fine-grinding hammer mills
  - 2. Pin mills
  - 3. Colloid mills
  - 4. Wood-pulp beaters
- *K.* Fluid-energy superfine mills:
  - 1. Centrifugal jet
  - 2. Opposed jet
  - 3. Jet with anvil
  - 4. Fluidized-bed jet

TABLE 20-7 Guide to Selection of Crushing and Grinding Equipment

Size-reduction operation	Hardness of material	Size* Range of feeds, in.† Max.	Range of feeds, in.† Min.	Range of products, in.† Max.	Range of products, in.† Min.	Reduction ratio‡	Types of equipment
Crushing:							
Primary	Hard	60	12	20	4	3 to 1	*A* to *B*
		20	4	5	1	4 to 1	
Secondary	Hard	5	1	1	0.2	5 to 1	*A* to *E*
		1.5	0.25	0.185 (4)	0.033 (20)	7 to 1	
	Soft	60	4	2	0.4	10 to 1	*C* to *G*
Grinding:							
Pulverizing:							
Coarse	Hard	0.185 (4)	0.033 (20)	0.023 (28)	0.003 (200)	10 to 1	*D* to *I*
Fine	Hard	0.046 (14)	0.0058 (100)	0.003 (200)	0.00039 (1250)	15 to 1	*H* to *K*
Disintegration:							
Coarse	Soft	0.5	0.065	0.023	0.003	20 to 1	*F, I*
Fine	Soft	0.156 (5)	0.0195 (32)	0.003 (200)	0.00039 (1250)	50 to 1	*I* to *K*

*85% by weight smaller than the size given.
†Sieve number in parentheses, mesh per inch
‡Higher reduction ratios for closed-circuit operations.
NOTE: To convert inches to millimeters, multiply by 25.4.

an impact crusher or a gyratory is best. Further information is given under each type of mill, and also in the subsection on crushed stone and aggregate.

JAW CRUSHERS

Design and Operation These crushers may be divided into two main groups (Fig. 20-21), the *Blake,* with a movable jaw pivoted at the top, giving greatest movement to the smallest lumps; and the *overhead eccentric,* which is also hinged at the top, but through an *eccentric-driven* shaft which imparts an elliptical motion to the jaw. Both types have a removable crushing plate, usually corrugated, fixed in a vertical position at the front end of a hollow rectangular frame. A similar plate is attached to the swinging movable jaw. The Blake jaw (Fig. 20-22) is moved through a knuckle action by the rising and falling of a second lever (pitman) carried by an eccentric shaft. The vertical movement is communicated horizontally to the jaw by double toggle plates. Because the jaw is pivoted at the top, the throw is greatest at the discharge, preventing choking.

Crushing angles in standard Allis-Chalmers-Svedala Blake-type machines generally are near 0.47 rad (27°) (see Fig. 20-21). The reduction ratios at minimum recommended settings and with straight jaw plates average about 8:1. Curved (or concave) jaw plates are designed to minimize choking.

The **overhead eccentric jaw crusher** (*Nordberg, Telsmith Inc., and Cedarapids*) falls into the second type. These are single-toggle machines. The lower end of the jaw is pulled back against the toggle by a tension rod and spring.

The choice between the two types of jaw crushers is generally dictated by the feed characteristics, tonnage, and product requirements (Pryon, *Mineral Processing,* Mining Publications, London, 1960; Wills, *Mineral Processing Technology,* Pergamon, Oxford, 1979.) Greater wear caused by the elliptical motion of the overhead eccentric and direct transmittal of shocks to the bearing limit use of this type to readily breakable material, although Cedarapids has reduced the elliptical wear effect by moving the bearing over the crushing chamber. Overhead eccentric crushers are generally preferred for crushing rocks with a hardness equal to or lower than that of limestone. Operating costs of the overhead eccentric are higher for the crushing of hard rocks, but its large reduction ratio is useful for simplified low-tonnage circuits with fewer grinding steps. Double-toggle type crushers cost about 50 percent more than similar overhead-eccentric-type crushers.

Comparison of Crushers The jaw crusher can accommodate the same size rocks as a gyratory, with lower capacity and also lower capital and maintenance costs, but similar installation costs. Therefore they are preferred when the crusher gape is more important than the throughput. If required throughput in tons/h is less than the square of the gape in inches, a jaw crusher is more economical (Taggart, *Handbook of Mineral Dressing,* Wiley, New York, 1945). Relining the gyratory requires more effort than for the jaw, and also more space above and below the crusher. Improved alloys have reduced the need for relining, however. Gyratories are preferred for larger throughputs. In metal mines continuity of operation favors gyratories over jaws because of their low maintenance. Quarries on the other hand can use hammer or other impact crushers, while maintenance is done on second shift.

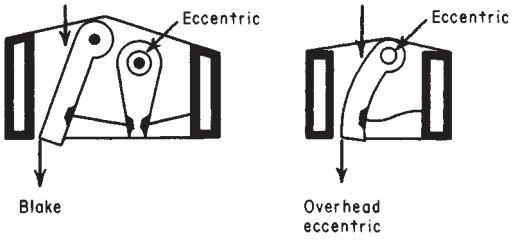


FIG. 20-21 Jaw-crusher designs.

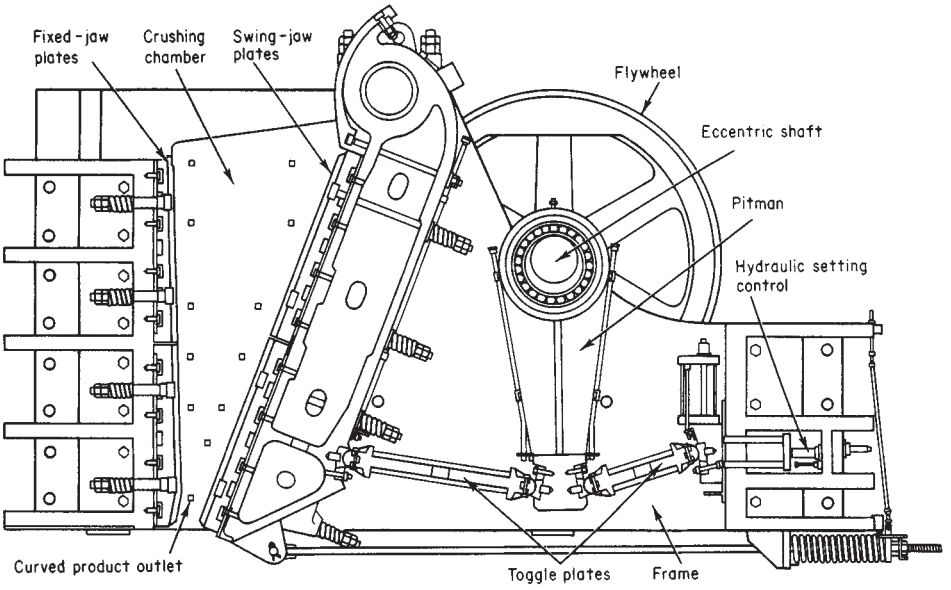


FIG. 20-22 Blake jaw crusher. (*Allis Mineral Systems Grinding Div., Svedala Industries, Inc.*)

Performance Jaw crushers are applied to the primary crushing of hard materials and are usually followed by other types of crushers. In smaller sizes they are used as single-stage machines. Jaw crushers are usually rated by the dimensions of their feed area. This depends on the width of the crushing jaws and the *gape*, which is the maximum distance between the fixed and movable jaws at the feed opening. The *setting* of a jaw crusher is the *closed* (or close) or the *wide opening* between the moving jaws at the outlet end, usually measured between tips of the corrugations. The reciprocating motion of the jaws causes the opening to vary between closed and wide, and the difference is the *throw*. Specifications are usually based on the closed settings. The setting is adjustable.

The throw of Blake jaw crushers is determined by the hardness of the ore as well as the size of the machine [Mollick et al., *Engineering & Mining J.*, **181**(6), 69–171 (1980)]. It may vary from ¼ in for hard but friable ores to 3 in for resilient material. The Big Bite jaw crusher (*Kue-Ken Div, Process Technology Inc.*) is a Blake double-toggle type in which the fulcrum pinion is positioned well over the center of the grinding chamber [Anon., *Quarry Management*, **18**(1), 25–7 (1991)]. This increases the throw at the top of the jaw opening, allowing it to better crush large rocks. It can be shipped in sections. Capacities of Kue-Ken jaw crushers (Blake type) are given in Table 20-8, including both standard and Big Bite types. Performance data of overhead eccentric crushers with straight jaw plates are given in Table 20-9.

Dragon single-toggle primary jaw crushers are supplied (by *Fives-Cail Babcock*) in eight sizes. The smallest is the MR53 with feed opening 550 × 350 mm and the largest is the MR200 with feed opening 2000 × 1600 mm, the corresponding capacities being from 15 to 800 ton/h. These units can be supplied fully mobile or on skid frames. The BCS series are extra heavy-duty crushers. High flywheel inertia enables them to accept large lumps of limestone and achieve throughputs up to 6000 ton/h. Pegson Telsmith in UK has a new single-toggle primary jaw crusher with roller bearings sized at 1000 × 800 mm. It is expected to be the first of a new line that incorporates the latest manufacturing techniques. Universal Engineering Corp. offers 27 sizes of overhead eccentric crusher, with long jaws and small nip angle to reduce rebound.

Smaller jaw crushers are available from Sturtevant Inc, with capacities of 1 to 10 hp (0.7 to 7 kW). Jaw settings range from ⅛ to 2.5 in (3 to 65 mm).

GYRATORY CRUSHERS

The development of improved supports and drive mechanisms has allowed gyratory crushers to take over most large hard-ore and mineral-crushing applications. The largest expense of these units is in relining them. Operation is intermittent; so power demand is high, but the total power cost is not great.

Design and Operation The gyratory crusher (see Fig. 20-23) consists of a cone-shaped pestle oscillating within a larger cone-shaped mortar or bowl. The angles of the cones are such that the width of the passage decreases toward the bottom of the working faces. The pestle consists of a mantle which is free to turn on its spindle. The spindle is oscillated from an eccentric bearing below. Differential motion causing attrition can occur only when pieces are caught simultaneously at the top and bottom of the passage owing to different radii at these points.

The circular geometry of the crusher gives a favorably small **nip angle** in the horizontal direction. The nip angle in the vertical direction is less favorable and limits feed acceptance. The vertical nip angle

TABLE 20-8 Performance Data for Blake Jaw Crushers

Model	Feed opening, in.	hp	Closed setting, in.	Capacity, ton/h	Weight, 1000 lb.	Max. r/min.
Standard 22	3 × 12	10	¼	2–5	3	400
			2	19–32		
54	8 × 24	15–25	¾	15–26	7	400
			3	59–88		
81	12 × 36	25–40	1	32–50	17	390
			3	95–135		
95	24 × 36	30–50	2	64–95	27	390
			6	195–270		
Big Bite 110	25 × 42	50–60	2	85–120	40	390
			5	205–275		
160	42 × 48	125–150	4	215–290	117	290
			10	520–770		
440	66 × 84	350–400	7	835–1310	455	210
			22	2625–4120		

To convert inches to millimeters, multiply by 2.54; to convert pounds to kilograms, multiply by 0.4535; to convert horsepower to kilowats, multiply by 0.746; and to convert tons per hour to kilograms per hour, multiply by 907.

TABLE 20-9 Performance Data for Overhead Eccentric Jaw Crushers*

			Capacity, tons/h								
			Setting, in.								
Crusher Size, in.	r/min.	hp	¾	1	1½	2	3	4	6	8	12
10 × 16	300	20–30	15	20	30	40	60				
12 × 36	275	60–75			65	85	130	175			
24 × 36	250	125–150					130	175	265		
30 × 42	250	125–175						200	300	400	610
54 × 60	200	350–450						290	440	580	880

*Cedar Rapids, CO. Div. of Raytheon Co., Pocket Reference Book, 13 ed., pp. 8–12, 1993.
Capacity can vary depending on breaking characteristics and compression strength of each: installed horsepower, size of feed, rate of feed, type of fall, and proper operating conditions.

is determined by the shape of the mantle and bowl liner; it is similar to that of a jaw crusher.

Primary crushers have a steep cone angle and a small reduction ratio. **Secondary** crushers have a wider cone angle; this allows the finer product to be spread over a larger passage area and also spreads the wear over a wider area. Wear occurs to the greatest extent in the lower, fine-crushing zone. These features are further extended in cone crushers; therefore secondary gyratories are much less popular than secondary cone crushers, but they can be used as primaries when quarrying produces suitable feed sizes.

The three general types of gyratory crusher are the **suspended-spindle,** the **supported-spindle,** and the **fixed-spindle** types. Primary gyratories are designated by the size of feed opening, and

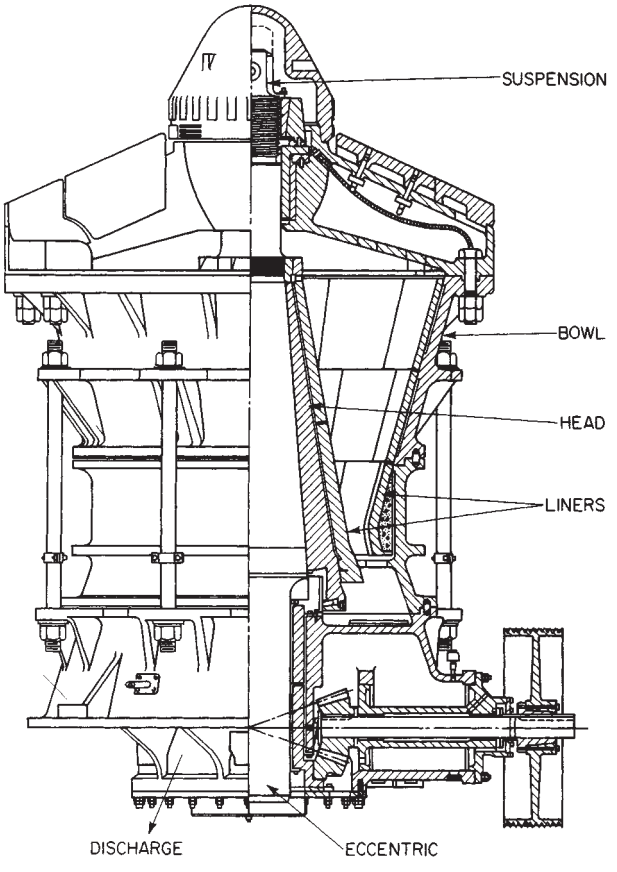


FIG. 20-23 Primary gyratory crusher with spider suspension. (*Nordberg, Inc.*)

secondary or reduction crushers by the diameter of the head in feet and inches. There is a close opening and a wide opening as the mantle gyrates with respect to the concave ring at the outlet end. The close opening is known as the close setting or the close-side setting or the closed-side setting, while the wide opening is known as the wide-side or open-side setting. Specifications usually are based on closed settings. The setting is adjustable by raising or lowering the mantle.

The length of the crushing stroke greatly affects the capacity and the screen analysis of the crushed product. A very short stroke will give a very evenly crushed product but will not give the greatest capacity. A very long stroke will give the greatest capacity, but the product will contain a wider product-size distribution.

Performance Crushing occurs through the full cycle in a gyratory crusher, and this produces a higher crushing capacity than a similar-sized jaw crusher, which crushes only in the shutting half of the cycle. Gyratory crushers also tend to be easier to operate. They operate most efficiently when they are fully charged, with the main shaft fully buried in charge. Power consumption for gyratory crushers is also lower than that of jaw crushers. These are preferred over jaw crushers when capacities of 800 Mg/h (900 tons/h) or higher are required.

Gyratories make a product with open-side settings of 5 to 10 in at discharge rates from 600 to 6000 ton/h, depending on size. Most manufacturers offer a throw from ¼ to 2 in. The throughput and power draw depend on the throw and the hardness of the ore, and on the amount of undersized material in the feed. Removal of undersize (which can amount to ⅓ of the feed) by a stationary grizzly can reduce power draw.

Crusher Product Sizes Table 20-10 relates product size to the discharge setting of the crusher in terms of the percent smaller than that size in the product. Size-distribution curves differ for various types of materials crushed, and a general set of curves is not valid.

Primary gyratories will accept feed directly from truck or railcar. Most manufacturers make both mechanical and hydraulically supported types. Figure 20-23 shows a Nordberg primary gyratory crusher with spider suspension. It is available in 1- to 1.5-m (42-, 48-, 54-, and 60-in) feed sizes. Table 20-11 gives capacity data for the Superior gyratory crusher (*Allis-Chalmers*).

Gyratory crushers that feature wide-cone angles are called **cone crushers.** These are suitable for secondary crushing, because crushing of fines requires more work and causes more wear; the cone shape provides more working area than primary or jaw crushers for grinding of the finer product. Crusher performance is harmed by sticky material in the feed, more than 10 percent fines in the feed smaller than the crusher setting, excessive feed moisture, feed-size segregation, uneven distribution of feed around the circumference, uneven feed control, insufficient capacity of conveyors and closed-circuit screens, extremely hard or tough feed material, and operation at less than recommended speed. Rod mills are sometimes substituted for crushing of tough ore, since they provide more easily replaceable metal for wear.

HP Series Cone Crushers (*Nordberg Inc.*) (Fig. 20-24) are available in four sizes. The previous standard- and short-head versions have been combined into one machine, with replaceable liner shapes corresponding to either version, adapted respectively to relatively coarse and fine grinding. In addition, the throw has been increased so as to

TABLE 20-10 Relation of Product Size to Discharge Setting of Crusher*

Setting measured on open side	Kind of feed	% of product passing a square opening equal to discharge setting of crusher			
		Limestone	Granite	Trap rock	Ores
Primary service:					
Jaw crusher†	Quarry-run	85–90	70–75	65–70	85–90
	Prescalped	80–85	65–70	60–65	80–85
Gyratory crusher	Quarry-run	85–90	75–80	65–70	85–90
	Prescalped	80–85	70–75	60–65	80–85
Secondary service:					
Gyratory crusher‡	Screened	85–90	80–85	75–80	85–90

*From "Crushing Theory and Practice," Allis-Chalmers Mfg. Co.
†Blake type, or crushers with equivalent speeds and throws: opening measured from tip of corrugations on one jaw plate to bottom of corrugations in opposing plate.
‡For standard, or reduction, types with nonchoking concaves. Single-toggle jaw product, on screened feed, will approximate that of gyratory-type secondary crushers with nonchoking concaves.

TABLE 20-11 Performance Data for Primary Gyratory Crushers*

Capacities for crushing limestone, tons/hr.

Crusher size	Approx. feed opening, in.	Gyrations per min.	Pinion r.p.m.	Max. hp.	Eccentric throw, in.	Open-side setting of discharge opening, in																		
						2½	3	3½	4	4½	5	5½	6	6½	7	7½	8	8½	9	9½	10	10½	11	11½	12
30–55	30 × 78	175	585	150	⅝	150	205	270	335	390	450	510												
					1¼				605	675	735	800												
42–65	42 × 108	150	497	265	1					540	660	790	920	1040	1170									
					1½								1040	1260	1490									
54–74	54 × 132	135	497	300	1							960	1040	1100	1160	1240	1330							
					1⅝										1950	2070	2210							
60–109	60 × 150	100	400	1000	1½													3250	3500	3750	4000	4250	4500	4750	5000

*Allis-Chalmers Corporation. To convert inches to millimeters, multiply by 2.514; to convert horsepower to watts, multiply by 746.

replace the previous Gyradisc models, designed to reduce wear by facilitating interparticle breakage with increased particle-bed depth. A built-in hydraulic motor unscrews the head for easy change-out of the liner. The feed opening ranges from 0.8 to 14.3 in depending on the mill size and the liner chosen. The drive shaft turns an eccentric, which causes the head to oscillate in the mantle, while a head ball resists vertical thrust. Bronze bearings withstand severe operating conditions, and labyrinth seals prevent bearing contamination. Hydraulic pistons allow remote or automated control of settings and release tramp iron.

Cone crushers can be operated in open circuit with capacities shown in Table 20-12, or in closed circuit in parallel with scalping screens for multistage size reduction, as Table 20-13 shows (the product sizes are not comparable). The feed should not contain more than

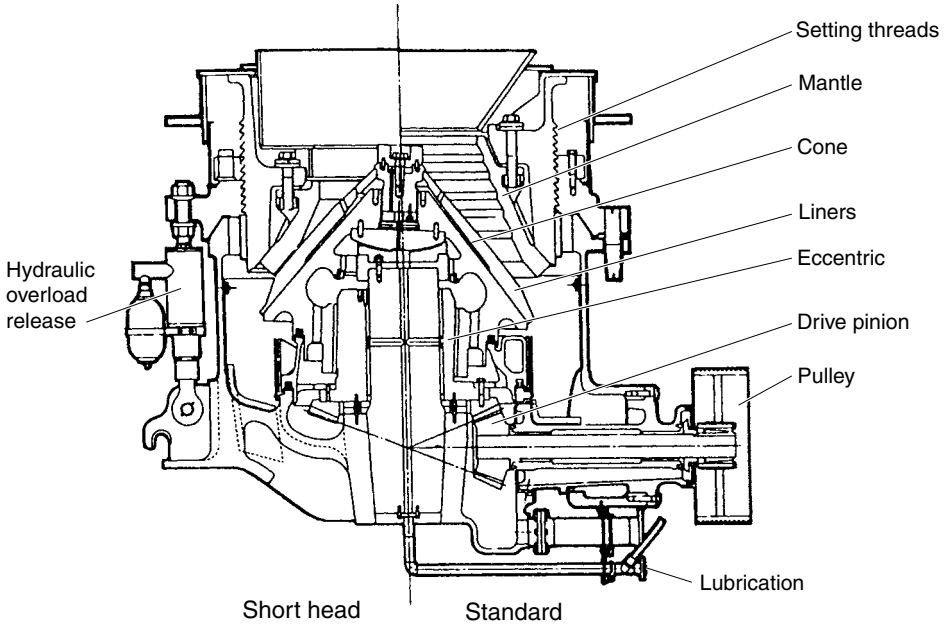


FIG. 20-24 HP700 cone crusher. (*Nordberg, Inc.*)

10 percent fines less than the discharge setting, else scalping screens should be used. A series of Waterflush Crushers is also available from Nordberg, which flush out fines and increase capacity with some feeds, and allow its use in closed circuit with wet ball and autogenous mills (qv). It can give products with 80 percent passing as small as 0.15 in.

The Eljay Rollercone crusher (*Cedarapids Eljay Div.*) uses a different drive principle: a wedge-shaped plate rotates on a ring of roller bearings under the crushing cone, causing it to oscillate. Low wear of these bearings maintains close tolerance of settings and hence of product size, and their overdesign results in long bearing life. A hydraulic-relief system passes larger pieces of tramp iron than spring-relief systems, while a hydraulic hold-down system allows quick changing of crusher-setting shims. The massive base frame directs compression forces to the product, reducing energy losses due to structural deflection of the members. The crusher is available in sizes from 36- to 66-in diameter. With standard head the capacity ranges from 36 to 580 ton/h at closed-side settings of ⅜ to 2 in; with a fine-crushing head the capacity ranges from 37 to 368 ton/h with closed-side setting of 1.4 to 1 in and recirculating rates from 18 to 30 percent.

Control of Crushers Lower-grade raw materials, higher energy costs, larger-scale operations, and more complex, capital-intensive plants make automatic control of size-reduction equipment more important (Suominen, 21st International Symposium—Applications of Computers and Operations Research in the Mineral Industry, 1011–1018). Benefits are: increased productivity, process stability and safety, improved recovery of mineral values, and reduced costs [Horst and Enochs, *Engineering & Mining J.*, **181**(6), 69–171 (1980)].

Improved sensors allow computer monitoring of the system for safety and protection of the equipment from damage. Sensors include lubrication-flow monitors and alarms, bearing-temperature sensors, belt scales, rotation sensors, and proximity sensors to detect ore level under the crusher. The latter prevent jamming of the output with too high an ore level, and protect the conveyor from impact of lumps with too low an ore level. Motion detectors assure that the conveyor is moving. Control applied to crusher systems including conveyors can facilitate use of mobile crushers in quarries and mines, since these can be controlled remotely by computer with reduced labor.

The objective of crusher control is usually to maximize crusher throughput at some specified product size, without overloading the crusher. Usually only three variables can be adjusted: feed rate, crusher opening, and feed size in the case of a secondary crusher. Four modes of control for a crusher are: (1) Setting overload control, where the gape setting is fixed except that it opens when overload occurs. A hardness change during high throughput can cause a power overload on the crusher, which control should protect against. (2) Constant power setting control, which maximizes throughput. (3) Pressure control, which provides settings that give maximum crusher force, and hence, also throughput. (4) Feeding-rate control, for smooth operation. Setting control influences mainly product size and quality, while feed control determines capacity. Flow must also be synchronized with the feed requirements of downstream processes such as ball mills, and improved crusher efficiency can reduce the load on the more costly downstream grinding.

ROLL CRUSHERS

Once popular for coarse crushing, these devices long ago lost favor to gyratory and jaw crushers because of their poorer wear characteristics with hard rocks. Roll crushers are still commonly used for both primary and secondary crushing of coal and other friable rocks such as oil shale and phosphate. The roll surface is smooth, corrugated, or toothed, depending on the application. *Smooth rolls* tend to wear ring-shaped corrugations that interfere with particle nipping, although some designs provide a mechanism to move one roll from side to side to spread the wear. *Corrugated rolls* give a better bite to the feed, but wear is still a problem. *Toothed rolls* are still practical for rocks of not too high silica content, since the teeth can be regularly resurfaced with hard steel by electric-arc welding. Toothed rolls are frequently used for crushing coal and chemicals. For further details, see edition 6 of this handbook.

The **capacity** of roll crushers is calculated from the ribbon theory, according to the following formula:

$$Q = dLs/2.96 \qquad (20\text{-}38)$$

where Q = capacity, cm^3/min; d = distance between rolls, cm; L = length of rolls, cm; and s = peripheral speed, cm/min. The denominator becomes 1728 in engineering units for Q in cubic feet per minute, d and L in inches, and s in inches per minute. This gives the theoretical capacity and is based on the rolls' discharging a continuous, solid uniform ribbon of material. The actual capacity of the crusher depends on roll diameter, feed irregularities, and hardness and varies between 25 and 75 percent of theoretical capacity.

Sturtevant two-roll crushers are available in capacities from 2 to 30 hp (1.5 to 22 kW). The gap is controlled by a hand-wheel. Rolls are hard-surfaced for wear resistance.

TABLE 20-12 Cone Crusher Capacity in Open Circuit, ton/h*

Mill	Feed opening +, in.	Motor hp	r/min	Closed-Side Discharge Setting, in						
				¼	⅜	½	¾	1	1.5	2
HP200	¾–7	150	1200	85	110	150	190	220	200	
HP500	¾–12	450	900	180	230	290	390	445	540	605
HP700	1½–14	600	850	300	370	425	600	675	845	975
MP1000	5–18	1000		600	750	900	1100	1200	1800	2400

*Nordberg Inc.—assumes feed weighing 100 lb/ft^3 and with a work index of 13.
Range covered by short-head and standard versions.

TABLE 20-13 Cone Crusher Capacity in Closed-Circuit, ton/h*

Mill	Top Size of Product from Screen (98% passing), in											
	¼		⅜		½		¾		1		1½	
	A	B	A	B	A	B	A	B	A	B	A	B
HP200	65	90	80	115	115	165	140	200	160	230	180	265
HP500	135	195	175	250	220	315	280	405	335	465	380	545
HP700	215	310	275	390	215	445	425	610	480	680	590	850
MP1000	320	480	980	720	630	800	840	1100	1000	1200		

*Nordberg Inc. Assumes feed weighing 100 lb/ft^3 and with a work index of 13.
A—Net finished product from screen.
B—Recirculating load.

ROLL PRESS

A novel comminution device, the **roll press,** has achieved commercial success [Schoenert, *International J. Mineral Processing,* **22,** 401–412 (1988)]. It is used for fine crushing, replacing the function of a coarse-ball mill or of tertiary crushers. Unlike ordinary roll crushers which crush individual particles, the roll press is choke fed and acts on a thick stream or ribbon of feed. Particles are crushed mostly against other particles, so wear is very low. Energy efficiency is also greater than in ball mills.

The product is in the form of agglomerated slabs. These are broken up either in a ball mill or an impact or hammer mill running at a speed too slow to break individual particles. Some materials may even deagglomerate from the handling that occurs in conveyors. Product-size distributions are shown in Fig. 20-25. Note that the press can handle a hard rock like quartz. Pressure in Fig. 20-25 is the calculated force-per-unit contact area in the nip. A large proportion of fines is produced, but a fraction of coarse material survives. This makes recycle necessary. From experiments to grind cement clinker –80 μm, as compression is increased from 100 to 300 MPa, the required recycle ratio decreases from 4 to 2.8. The energy required per ton of throughput increases from 2.5 to 3.5 kWh/ton. These data are for a 200-mm diameter pilot-roll press.

Status of 150 installations in the cement industry are reviewed [Strasser et al., *Rock Products,* **92**(5), 60–72 (1989)]. In cement-clinker milling, wear is usually from 0.1 to 0.8 g/ton, and for cement raw materials it is between 0.2 and 1.2 g/ton, whereas it may be 20- to 40-in ball mills. New surface of 100 to 130 cm^2/g is produced with cement. The size of the largest feed particles should not exceed 0.04 × roll diameter (D) according to Schoenert (loc. cit.). However, it has been found [Wuestner et al., *Zement-Kalk-Gips,* **41**(7), 345–353 (1987); English edition, 207–212] that particles as large as 3–4 times the roll gap may be fed to an industrial press. Particles receive preliminary breakage at the top of the nip.

The hybrid circuit in Fig. 20-26 has proven most versatile, and can increase capacity of an existing ball-mill circuit by 30 to 100 percent. Recycling the rock as in the hybrid flow sheet reduces the need for coarse-ball milling.

Roll presses are now manufactured by most cement-equipment manufacturers, for example Krupp-Polysius AG. For drives up to 1200 kW they are equipped with V-belt drives, allowing speed to be changed. Rolls in one particular crusher are 48 inches (1200 mm) in diameter and 30 inches (700-mm) wide and each weighs 90 tons. Machines with up to 2500 kW installed power and 1000 ton/h (900 tonne/h) capacity have been installed. The largest presses can supply feed for four or five ball mills.

Operating experience (Wuestner et al., loc. cit.) has shown that roll diameters about 1 m are preferred, as a compromise between production rate and stress on the equipment. The press must be operated choke fed, with a substantial depth of feed in the hopper; otherwise it will act like an ordinary roll crusher.

The advent of the roll press has greatly improved the economy of cement milling. More information is given later under cement.

IMPACT BREAKERS

Impact breakers include heavy-duty hammer crushers and rotor impact breakers. Fine hammer mills are described in a subsequent subsection.

Not all rocks shatter well by impact. Impact breaking is best suited for the reduction of relatively nonabrasive and low-silica-content materials such as limestone, dolomite, anhydrite, shale, and cement rock, the most popular application being on limestone.

Hammer Crusher (Fig. 20-27) Pivoted hammers are mounted on a horizontal shaft, and crushing takes place by impact between the hammers and breaker plates. Heavy-duty hammer crushers are frequently used in the quarrying industry, for processing municipal solid waste, and scrap automobiles.

These crushers are of two types, with and without grates or screens. The bottom of the **Pennsylvania reversible impactor** (Fig. 20-27) is open, and the sized material passes through almost instantaneously. Particles acquire high velocities, and this leads to little control on particle size and a much higher proportion of fines than slow-speed crushers. A product-size distribution curve (*Handbook of Crushing,* Pennsylvania Crusher Corp, 1994) shows the following for crushing of minus 10-in subbituminous coal from Wyoming: 92 percent minus 2 in, 48 percent minus 0.53 in, 15 percent minus 10 mesh/in.

In the second type of mill (Fig. 20-28), a cylindrical grating is provided beneath the rotor for product discharge. Some hammer crushers are symmetrically designed so that the direction of rotation can be reversed to distribute wear evenly on the hammer and breaker plates. When such a **Pennsylvania nonreversible hammermill** is used for reduction, material is broken first by impact against hammers and then by rubbing action (attrition) against screen bars. Performance data of Pennsylvania reversible hammer mills are shown in Table 20-14.

Sturtevant Inc. produces three sizes of screen-type hammermills with 5 to 50 hp (4 to 37 kW) capacity, suitable for recycle of glass and

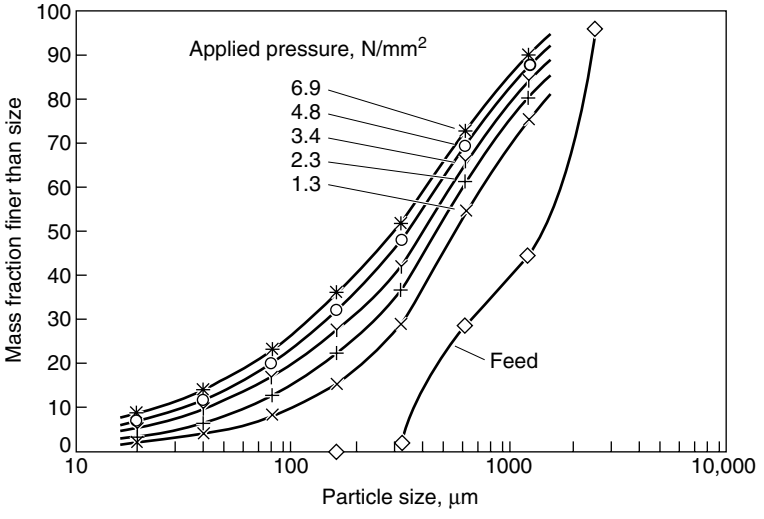


FIG. 20-25 Size distribution of roll-press products. Feed is quartz, 300–2500 μm, dry. [*Schonert,* International J. Mineral Processing, **22,** *401–412 (1988).*]

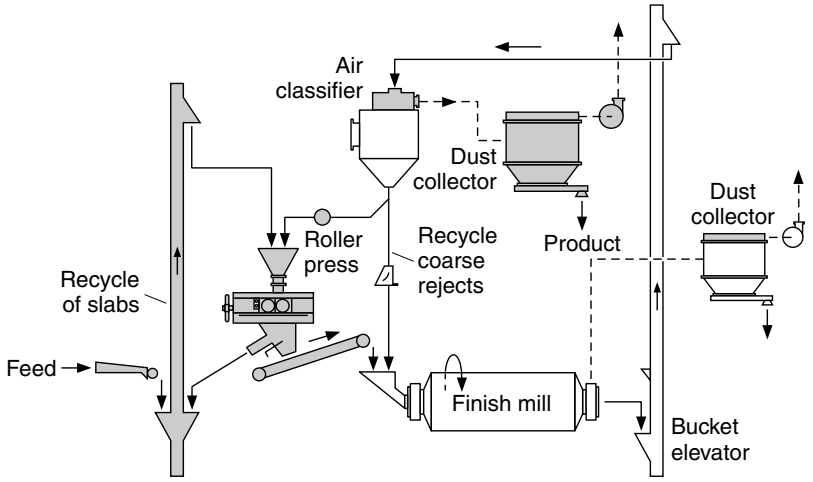


FIG. 20-26 Hybrid flow sheet to combine a roll press and ball mill with a classifier. (*Conroy, 31st IEEE Cement Industry Technical Conference, 509–542, 1988. Copyright IEEE.*)

wastes, and for mineral processing. **Jeffrey hammermills** (*Jeffrey Div, Indresco Inc.*) are available with screen grates having capacities from 50 to 140 ton/h (135 to 350 Mg/h) for a product with top size 1.75 in (45 mm). The screenless, reversible type is also available.

Each hammer may weigh several hundred kilograms. Speed varies between 500 to 1800 r/min, depending on the size of the machine.

Rotor Impactors The rotor of these machines is a cylinder to which is affixed a tough steel bar. Breakage can occur against this bar or on rebound from the walls of the device. Free impact breaking is the principle of the rotor breaker, and it does not rely on pinch crushing or attrition grinding between rotor hammers and breaker plates.

The result is a high reduction ratio and elimination of secondary and tertiary crushing stages. The investment cost may be a third of that for a two-stage jaw and gyratory crusher plant producing 180 Mg/h (200 tons/h) and half for a plant crushing 540 Mg/h (600 tons/h) [Godfrey, *Quarry Managers' J.*, 405–416 (October 1964)].

By adding a screen on a portable mounting, a complete, compact mobile crushing plant of high capacity and efficiency for use in any location is provided.

The peripheral speed of the rotors manufactured by *KHD Humboldt Wedag* is 34 m/sec; the 52-ton rotor can handle a lump as large as 8 ton. Controllers stop the feeder if rotor speed drops below 75 percent of normal [Schaefer and Gallus, *Zement-Kalk-Gips,* **41**(10), 486–492 (1988); English ed., 277–280].

Pennsylvania Crusher Corp. offers a variety of impactor types: granulators, Bradford breakers, roll crushers, and jaw crushers. (See Table 20-15.)

The **ring-type granulator** (*Pennsylvania Crusher Corp.*) features a rotor assembly with loose crushing rings, held outwardly by centrifugal force, which chop the feed. It is suitable for highly friable materials which may give excessive fines in an impact mill. For example, bituminous coal is ground to a product below 2 cm (¾ in). They have also been successfully used to grind abrasive quartz to sand size, due to the ease of replacement of the ring impact elements.

Cage Mills The **Stedman disintegrator** (*Stedman Machine Co.*), commonly referred to as a cage mill, is used for crushing quarry rock, phosphate rock, and fertilizer and for disintegrating clays, colors, press cake, and bones. Cages of one, two, three, four, six, and eight rows, with bars of special alloy steel, revolving in opposite directions, produce a powerful impact action that pulverizes many materials. (See Fig. 20-29.)

The life of a cage may be a few months and may produce 9000 Mg (10,000 tons) of quarry rock. A gray-iron cage is used for alumina grinding, with metal particles removed magnetically. The advantage of

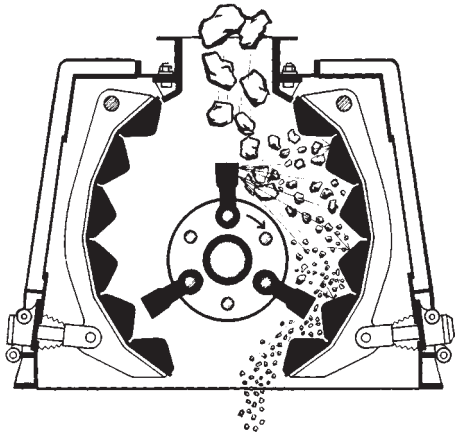


FIG. 20-27 Reversible impactor. (*Pennsylvania Crusher Corp.*)

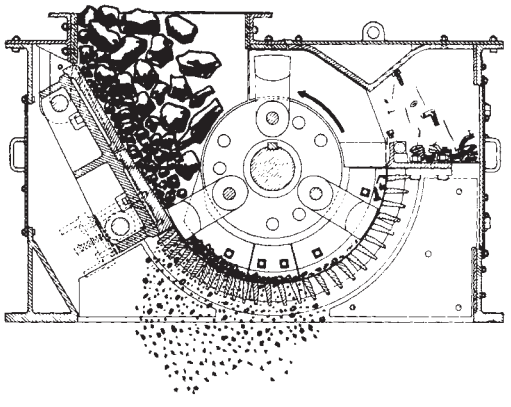


FIG. 20-28 Nonreversible hammermill (*Pennsylvania Crusher Corp.*)

TABLE 20-14 Performance Data for Reversible Hammer Mills

Model no.	Rotor dimensions, in	Maximum feed size, in	Maximum speed, r/min	hp	Capacity, tons/h
505	30 × 30	2½	1200	100–200	40–60
605	36 × 30	4	1200	200–300	80–100
708	42 × 48	8	900	300–550	140–180
815	48 × 90	10	900	900–1200	330–400
1014	60 × 84	12	720	1100–1500	450–500
1217	72 × 102	14	600	1550–2000	620–685
1221	72 × 126	14	600	1900–2500	760–850

NOTE: To convert inches to centimeters, multiply by 2.54; to convert horsepower to kilowatts, multiply by 0.746; and to convert tons per hour to megagrams per hour, multiply by 0.907.

TABLE 20-15 Performance of Dual-Rotor Impact Breakers

Model no.	Feed opening, in	Speed, r/min	hp	Hammer weight, lb	Product size, in	Capacity, tons/h
3648	36 × 48	550–990	250–300	300	2	300
4850	48 × 50	550–990	300–400	400	3	500
5462	54 × 62	480–750	400–500	500	4–5	700
6072	60 × 72	300–600	500–600	600	5–6	1200

To convert pounds to kilograms, multiply by 0.4535; to convert inches to centimeters, multiply by 2.54; to convert horsepower to kilowatts, multiply by 0.746; and to convert tons per hour to megagrams per hour, multiply by 0.907.

multiple-row cages is the achievement of a greater reduction ratio in a single pass.

These features and the low cost of the mills make them suitable for medium-scale operations where complicated circuits cannot be justified. The maximum feed size is 20 cm (8 in), and the product size may be as fine as 325 mesh.

Prebreakers Aside from the normal problems of grinding, there are special procedures and equipment for breaking large masses of feed to smaller sizes for further grinding. There is the breaking or shredding of bales, as with rubber, cotton, or hay, in which the compacted mass does not readily come apart. There also is often caking in bags of plastic or hygroscopic materials which were originally fine. Although crushers are sometimes used, the desired size-reduction ratio often is not obtainable. Furthermore, a lower capital investment may result through choosing a less rugged device which progressively attacks the large mass to remove only small amounts at a time. In structure such a device comprises a toothed rotating shaft in a casing.

Prater Industries, Inc., offers a double roll with heavy-duty teeth as a precrusher feeder. The **Mikro roll crusher** (*Hosokawa Micron Powder Systems*) serves as grinder or prebreaker and is of similar type. The **Rietz prebreaker** differs somewhat from these.

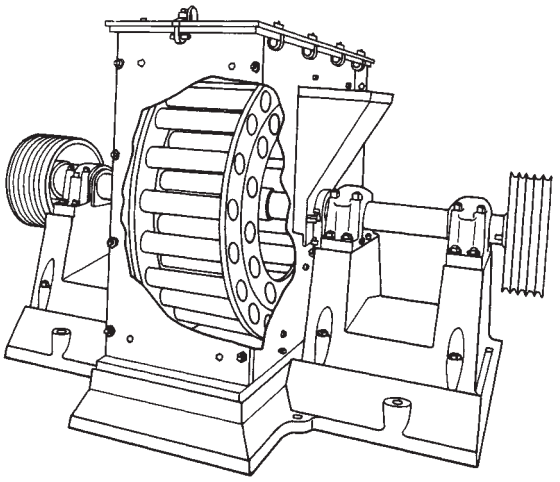


FIG. 20-29 Two-cage disintegrator. (*Stedman Machine Co.*)

Precision Cutters and Slitters Often it becomes desirable to reduce the size of a solid mass to regular smaller sizes.

Precision knife cutters differ from random cutting mills in that a feeder is synchronized with the knives. This ensures the exact size, whether it be slit widths in a sheet, fiber length from a strand, or both width and length from a sheet, as in dicing. In the **Giant dicing cutter,** the sheet stock is first slit lengthwise with opposing sets of circular knives. The slit strands then pass between pressure rolls to a rotary cutter which operates against an adjustable bed knife. Capacities range up to 18 Mg/h (20 tons/h), with sheet stock up to 60 cm (24 in) wide.

PAN CRUSHERS

Design and Operation The pan crusher (Fig. 20-30) consists of one or more grinding wheels or mullers revolving in a pan; the pan may remain stationary and the mullers be driven, or the pan may be driven while the mullers revolve by friction. The mullers are made of tough alloys such as Ni-Hard. Iron scrapers or plows at a proper angle feed the material under the mullers.

The **Chambers dry pan** (*Bonnot Co.*) uses air cylinders to regulate the grinding pressure under each of the muller tires from 33,000 to 90,000 N (7500 to 20,000 lb).

The pan bottom rotates and has a central solid crushing ring as well as an outer ring of screen plates with openings from 0.16 to 1.3 cm (1/16 to ½ in). In some instances a solid pan bottom is used in place of a perforated screen bottom, and the ground material is discharged through a slot in the rim.

Performance The dry pan is useful for crushing medium-hard and soft materials such as clays, shales, cinders, and soft minerals such as barites. Materials fed should normally be 7.5 cm (3 in) or smaller, and a product able to pass No. 4 to No. 16 sieves can be delivered, depending on the hardness of the material.

High reduction ratios with low power and maintenance are features of pan crushers.

The Chambers dry pan is available from 1.8 to 3 m (6 to 10 ft) pan diameter with mullers ranging from 0.71 to 1.6 m (28 to 62 in) in diameter with 13- to 46-cm (5- to 18-in) face. Power ranges from 11 to 75 kW (15 to 100 hp) or from 0.8 to 4 kW/Mg (1 to 5 hp/ton) of product. Production rate varies from 1 to 54 Mg/h (1 to 60 tons/h) according to pan size and hardness of material as well as fineness of feed and product.

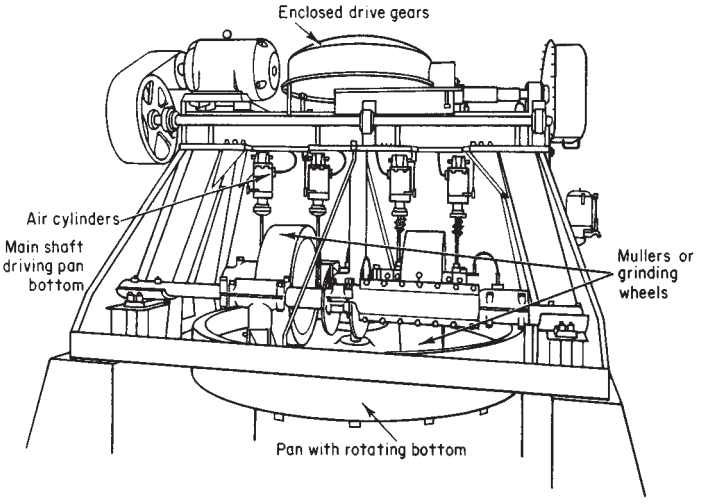


FIG. 20-30 Chambers 10-ft, 100-hp dry pan. (*Bonnot Co.*)

The **wet pan** is used for developing plasticity or molding qualities in ceramic feed materials. The abrasive and kneading actions of the mullers blend finer particles with the coarser particles as they are crushed (Greaves-Walker, *Am. Refract. Inst. Tech. Bull.* **64,** 1937), and this is necessary so that a high packing density can be achieved to result in strength.

TUMBLING MILLS

Ball, pebble, rod, tube, and compartment mills have a cylindrical or conical shell, rotating on a horizontal axis, and are charged with a grinding medium such as balls of steel, flint, or porcelain or with steel rods. The **ball mill** differs from the tube mill by being short in length; its length, as a rule, is not far from its diameter (Fig. 20-31). Feed to ball mills can be as large as 2.5 to 4 cm (1 to 1½ in) for very fragile materials, although the top size is generally 1 cm (½ in). Most ball mills operate with a reduction ratio of 20 to 200:1. The largest balls are typically 13 cm (5 in) in diameter.

The tube mill is generally long in comparison with its diameter, uses smaller balls, and produces a finer product. The compartment mill consists of a cylinder divided into two or more sections by perforated partitions; preliminary grinding takes place at one end and finish grinding at the discharge end. These mills have a length-to-diameter ratio in excess of 2 and operate with a reduction ratio of up to 600:1. Rod mills deliver a more uniform granular product than other revolving mills while minimizing the percentage of fines, which are sometimes detrimental.

The **pebble mill** is a tube mill with flint or ceramic pebbles as the grinding medium and may be lined with ceramic or other nonmetallic liners. The **rock-pebble mill** is an autogenous mill in which the

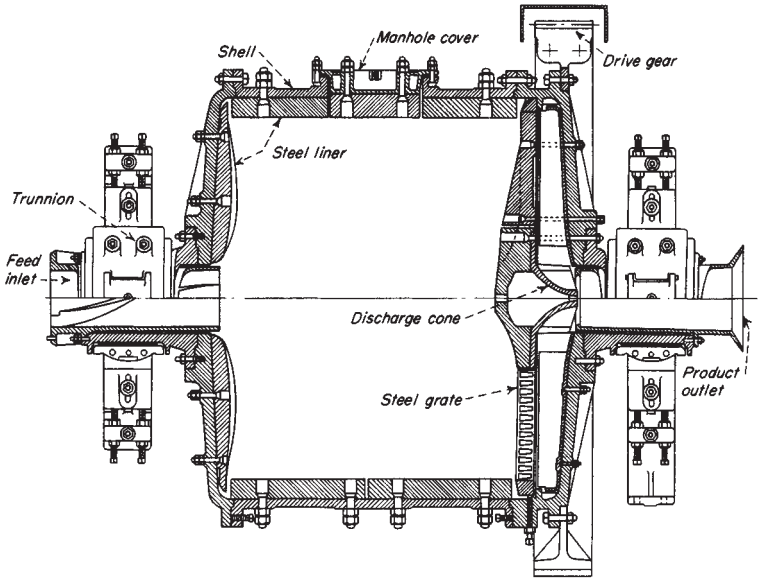


FIG. 20-31 Marcy grate-type continuous ball mill. (*Allis Mineral Systems, Svedala Inc.*)

medium consists of larger lumps scalped from a preceding step in the grinding flow sheet.

Design The conventional type of **batch mill** consists of a cylindrical steel shell with flat steel-flanged heads. Mill length is equal to or less than the diameter [Coghill, De Vaney, and O'Meara, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, **112,** 79 (1934)]. The discharge opening is often opposite the loading manhole and for wet grinding usually is fitted with a valve. One or more vents are provided to release any pressure developed in the mill, to introduce inert gas, or to supply pressure to assist discharge of the mill. In dry grinding, the material is discharged into a hood through a grate over the manhole while the mill rotates. Jackets can be provided for heating and cooling.

Material is fed and discharged through hollow trunnions at opposite ends of **continuous mills** (Fig. 20-31). A grate or diaphragm just inside the discharge end may be employed to regulate the slurry level in wet grinding and thus control retention time. In the case of **air-swept mills,** provision is made for blowing air in at one end and removing the ground material in air suspension at the same or other end.

Ball mills usually have **liners** which are replaceable when they wear. Optimum liner shapes which key the ball charge to the shell and prevent slippage are illustrated in Fig. 20-32. Special operating problems occur with smooth-lined mills owing to erratic slip of the charge against the wall. At low speeds the charge may **surge** from side to side without actually tumbling; at higher speeds tumbling with **oscillation** occurs. The use of lifters prevents this [Rose, *Proc. Inst. Mech. Eng.* (*London*), **170**(23), 773–780 (1956)]. Power consumption in a smooth mill depends in a complex way on operating conditions such as feed viscosity, whereas it is more predictable in a mill with lifters [Kitchener and Clarke, *Br. Chem. Eng.*, **13**(7), 991 (1968)].

Plant data on an 8-ft diameter rod mill showed that when smooth liners were replaced with lifter bars spaced 300 mm (12 in) apart, liner wear decreased by 13-fold, production increased 50 percent, and power per ton decreased by 34 percent [Howat and Vermeulen, *Journal South African Institute Mining and Metallurgy,* **86,** 251–259 (July 1986)]. When a smooth-walled ball mill was fitted with lifter bars the production of –75 μm material increased 8 percent and the power/ton decreased 10 percent. Plant tests confirmed previous results [Meaders and McPherson, *Mining Engineering,* **16,** 81–84 (Sept. 1964)] that optimum lifter bar spacing is from 3 to 5 times bar height.

Liner wear increases with the size, hardness, and sharpness of feed more than with ball size. The hardness of manganese steel corresponds to softer types of ore, while Nihard is about the same as magnetite [Moore et al., *International J. of Mineral Processing,* **22,** 313–343 (1983)]. Quartz and pyrite are considerably harder than any metals used. Rubber, being resilient, is less affected by ore hardness, and therefore has the advantage with harder ores. Low-charge volume below 35 percent results in increased wear since the liners are not protected by a covering of ore. Several studies indicate that wear increases at least proportional to the square of mill speed in percent of critical.

Both all-rubber liners, and rubber liners with metal lifter bars are currently used in large ball mills [McTavish, *Mining Engineering,* **42,** 1249–1251 (Nov. 1990)]. Both types (Fig. 20-32) have rubber-liner plates, separated and held in place by lifter bars. Rubber liners have the following advantages: Abrasion and impact resistance, 15 percent lower weight than steel, which makes replacement easier, lower noise, and tight sealing against the shell.

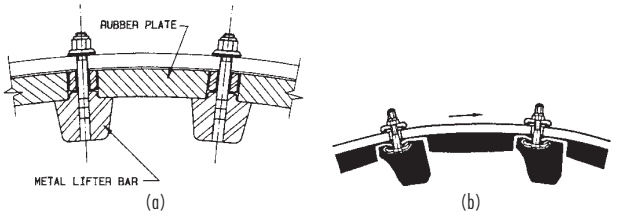


FIG. 20-32 Types of ball-mill liners: (*a*) combination liner [McTavish, *Mining Engineering,* **42,** 11, 1249–1251 (1990) Exton Industries, Inc.]; (*b*) all-rubber liner [Moller and Brough, *Mining Engineering,* **41,** 8, 849–853 (1989) Skega Ltd.].

The dimensions and spacing of rubber lifter bars are critical to good operation and wear resistance. Figure 20-32 shows rubber lifters with a spacing formula recommended by Moller and Brough [*Mining Engineering,* **41,** 849–853 (Aug. 1989)]. Lifters must be at least as high as the ball radius, to key the ball charge and assure that the balls fall into the toe area of the mill [Powell, *International J. Mineral Processing,* **31,** 163–193 (1991)].

The flexibility of rubber is helpful in discharge grates. Each time the grate dips into the slurry it flexes, tending to work out particles stuck in the grate holes. Metal frames support the rubber while leaving areas with holes free to flex. The grate is backed up by lifter bars which lift the slurry into the discharge trommel.

Grinding balls can be made of forged steel, cast steel, or cast iron. (See under Wear for more information on alloys.)

Pebble mills are frequently lined with nonmetallic materials when iron contamination would harm a product such as a white pigment or cement. Belgian silex (silica) or porcelain block are popular linings. Silica linings and ball media have proved to wear better than other nonmetallic materials. The higher density of silica media increases the production capacity and power draft of a given mill.

Capacities of pebble mills are generally 30 to 50 percent of the capacity of the same size of ball mill with steel grinding media and liners; this depends directly on the density of the media.

Smaller mills, up to about 0.19-m^3 (50-gal) capacity, are made in one piece with a cover. U.S. Stoneware Co. makes these in wear-resistant Burundum-fortified ceramic and also makes larger three-piece units, in a metal protective case, up to 0.8-m^3 (210-gal) capacity. A handbook on pebble milling is available from Paul O. Abbe, Inc., Little Falls, NJ.

Operation **Cascading** and **cataracting** are the terms applied to the motion of grinding media. The former applies to the rolling of balls or pebbles from top to bottom of the heap, and the latter refers to the throwing of the balls through the air to the toe of the heap.

The criterion by which the ball action in mills of various sizes may be compared is the concept of **critical speed.** It is the theoretical speed at which the centrifugal force on a ball in contact with the mill shell at the height of its path equals the force on it due to gravity:

$$N_c = 42.3/\sqrt{D} \qquad (20\text{-}39)$$

where N_c is the critical speed, r/min, and D is diameter of the mill, m (ft), for a ball diameter that is small with respect to the mill diameter. The numerator becomes 76.6 when D is expressed in feet.

Actual mill speeds range from 65 to 80 percent of critical. It might be generalized that 65 to 70 percent is required for fine wet grinding in viscous suspension and 70 to 75 percent for fine wet grinding in low-viscosity suspension and for dry grinding of large particles up to 1-cm (½-in) size. The speeds might be increased by 5 percent of critical for unbaffled mills to compensate for slip.

The chief factors determining the size of **grinding balls** are fineness of the material being ground and maintenance cost for the ball charge. A coarse feed requires a larger ball than a fine feed.

The need for a calculated ball-size feed distribution is open to question; however, methods have been proposed for calculating a rationed ball charge [Bond, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, **153,** 373 (1943)].

The recommended optimum size of makeup rods and balls is [Bond, *Min. Eng.*, **10,** 592–595 (1958)]

$$D_b = \sqrt{\frac{X_p E_i}{K n_r}} \sqrt{\frac{\rho_s}{\sqrt{D}}} \qquad (20\text{-}40)$$

where D_b = rod or ball diameter, cm (in); D = mill diameter, m (ft); E_i is the work index of the feed; n_r is speed, percent of critical; ρ_s is feed specific gravity; and K is a constant = 214 for rods and 143 for balls. The constant K becomes 300 for rods and 200 for balls when D_b and D are expressed in inches and feet respectively. This formula gives reasonable results for production-sized mills but not for laboratory mills. The ratio between the recommended ball and rod sizes is 1.23.

A graded charge of rods results from wear in a rod mill. **Rod diameter** may range from 10 to 2.5 cm (4 to 1 in), for example. A new rod load usually is patterned after a used one found to give good results. The maximum length of a rod mill appears to be 20 ft, because longer rods tend to twist and bend.

Tumbling-Mill Circuits Tumbling mills may be operated in **normal closed circuit,** as shown in Fig. 20-45 or 20-59, or in **reverse arrangement** in which the feed passes through the classifier before entering the mill (see secondary mill in Fig. 20-44 or 20-59).

Material and Ball Charges The load of a grinding medium can be expressed in terms of the percentage of the volume of the mill that it occupies; i.e., a bulk volume of balls half filling a mill is a 50 percent ball charge. The void space in a static bulk volume of balls is approximately 41 percent. Since the medium expands as the mill is rotated, the actual running volume is unknown.

Simple relationships govern the amount of balls and voids in the mill. The weight of balls = $\rho_b \varepsilon_b V_m$, where ρ_b = bulk density of balls, g/cm^3 (lb/ft^3); ε_b = apparent ball filling fraction; and V_m = volume of mill = $\pi D^2 L/4$. Steel balls have a bulk density of approximately 4.8 g/cm^3 (300 lb/ft^3); stone pebbles, 1.68 g/cm^3 (100 lb/ft^3); and alumina balls, 2.4 g/cm^3 (150 lb/ft^3).

The amount of material in a mill can be expressed conveniently as the ratio of its volume to that of the voids in the ball load. This is known as the **material-to-void ratio.** If the solid material and its suspending medium (water, air, etc.) just fill the ball voids, the M/V ratio is 1, for example. Grinding-media loads vary from 20 to 50 percent in practice, and M/V ratios are usually near 1.

The material charge of continuous mills called the **holdup** cannot be set directly but is indirectly determined by operating conditions. There is a maximum throughput rate that depends on the shape of the mill, the flow characteristics of the feed, the speed of the mill, and the type of feed and discharge arrangement. Above this rate the holdup increases unstably.

The holdup of material in a continuous mill determines the mean residence time, and thus the extent of grinding. Gupta et al. [*International J. Mineral Processing,* **8,** 345–358 (Oct. 1981)] analyzed published experimental data on a 40 × 40-cm grate discharge laboratory mill, and determined that holdup was represented by $H_w = (4.020 - 0.176\ \mathrm{WI})F_w + (0.040 + 0.01237\ \mathrm{WI})S_w - (4.970 + 0.395\ \mathrm{WI})$, where WI is Bond work index based on 100 percent passing a 200-mesh sieve, F_w is the solids feed rate in kg/min, and S_w is weight percent solids in the feed. This represents experimental data for limestone, feldspar, sulfide ore, and quartz. The influence of WI is believed to be due to its effect on amount of fines present in the mill. Parameters that did not affect H_w are specific gravity of feed material, and feed size over the narrow range studied.

Sufficient data was not available to develop a correlation for overflow mills, but the data indicated a linear variation of H_w with F as well.

The mean residence time τ (defined as H_w/F) is the most important parameter, since it determines the time over which particles are exposed to grinding. Measurements on several industrial mills (Weller, *Automation in Mining Mineral and Metal Processing,* 3d IFAC Symposium, 303–309, 1980) (measured on the water, not the ore) showed that the maximum mill filling was about 40 percent, and the maximum flow velocity through the mill is 40 m/h.

Swaroop et al. [*Powder Technology,* **28,** 253–260 (Mar.–Apr. 1981)] found that the material holdup is higher and the vessel dispersion number $D\tau/L^2$ (see subsection on Continuous Mill Simulation) is lower in the rod mill than in the ball mill under identical dimensionless conditions. This indicates that the known narrow-product-size distribution from rod mills is partly due to less mixing in the rod mill, in addition to different breakage kinetics.

The holdup in grate-discharge mills depends on the grate openings. Kraft et al. [*Zement-Kalk-Gips International,* **42**(7), 353–9 (1989); English edition, 237–9] measured the effect of various hole designs in wet milling. They found that slots tangential to the circumference gave higher throughput and therefore lower holdup in the mill. Total hole area had little effect until the feed rate was raised to a critical value (30 m/h in a mill 0.26 m diam × 0.6 m long); above this the larger area led to lower holdup. The open area is normally specified between 3 and 15 percent, depending on the number of grinding chambers and other conditions. The slots should be 1.5 to 16 mm wide, tapered toward the discharge side by a factor of 1.5 to 2 to prevent blockage by particles.

Dry versus Wet Grinding The choice between wet and dry grinding is generally dictated by the end use of product. If the presence of liquid with the finished product is not objectionable or the feed is moist or wet, wet grinding generally is preferable to dry grinding, but power consumption, liner wear, and capital costs determine the choice. Other factors that influence choice are the performance of subsequent dry or wet classification steps, the cost of drying, and the capability of subsequent processing steps for handling a wet product.

The net production in wet grinding in the Bond grindability test varies from 145 to 200 percent of that in dry grinding depending on mesh [Maxson, Cadena, and Bond, *Trans. Am. Int. Min. Metall. Pet. Eng.,* **112,** 130–145, 161 (1934)]. Ball mills have a large field of application for wet grinding in closed circuit with size classifiers, which also perform advantageously wet.

In fine dry grinding, surface forces come into action to cause cushioning and ball coating with a less efficient use of energy. Grinding-media and liner-wear consumption per ton of ground product is lower for a dry-grinding system. However, power consumption for dry grinding is about 30 percent larger than for wet grinding. Dry grinding requires the use of dust-collecting equipment.

In **wet ball milling** the grinding rate increases with solids content up to 70 wt % (35 vol %), as Fig. 20-33 shows, due to pulp rheology. Examination of gouge marks indicated that most breakage was by impact of balls on particles rather than by abrasion.

The **rheological properties** of the slurry affect the grinding behavior in ball mills. Rheology depends on solids content, particle size, and mineral chemical properties [Kawatra and Eisele, *International J. Mineral Processing,* **22,** 251–259 (1988)]. Up to 50 percent solids by volume a mineral slurry exhibits dilatent behavior, i.e. shear stress increases more than proportionate to shear rate. Above 50 percent it becomes pseudoplastic, i.e., it exhibits a yield value (Austin, Klimpel, and Luckie, *Process Engineering of Size Reduction: Ball Milling,* AIME, 1984). Above the yield value the grinding rate decreases, and this is believed to be due to adhesion of grinding media to the mill wall causing centrifuging [Tangsatitkulchai and Austin, *Powder Technology,* **59**(4), 285–293 (1989)]. Maximum power draw and fines production are achieved when the solids content is just below that which produces the critical yield.

The solids concentration in a pebble-mill slurry should be high enough to give a slurry viscosity of at least 0.2 Pa·s (200 cP) for best grinding efficiency [Creyke and Webb, *Trans. Br. Ceram. Soc.,* **40,** 55

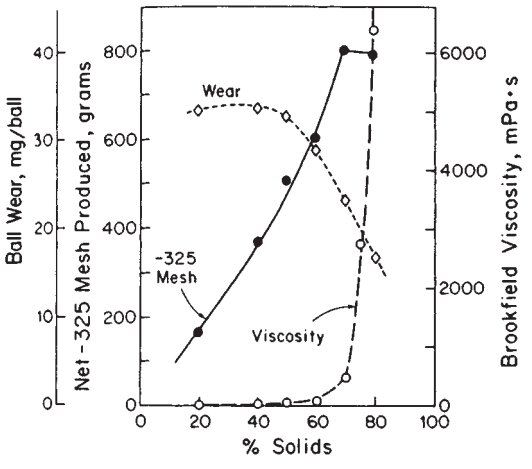


FIG. 20-33 Effect of percent solids on the wear of mild steel balls, net weight of 325 mesh material produced, and pulp viscosity after grinding magnetic taconite for 60 min [*Iwasaki et al.,* International J. Mineral Processing, **22,** *345–360 (1988).*]

(1941)], but this may have been required to key the charge to the walls of the smooth mill used.

Since viscosity increases with amount of fines present, mill performance can often be improved by closed-circuit operation to remove fines. Chemicals such as surfactants allow the solids content to be increased without increasing the yield value of the pseudoplastic slurry, allowing a higher throughput. They may cause foaming problems downstream, however. Increasing temperature lowers the viscosity of water, which controls the viscosity of the slurry under high-shear conditions such as those encountered in the cyclone, but does not greatly affect chemical forces. Slurry viscosity can be most directly controlled by controlling solids content. To control viscosity it is necessary to measure the viscosity on line. Kawatra and Eisele (loc. cit.) have described viscometers that can measure viscosity of a flowing slurry stream with high-solids content. A satisfactory spindle type operates in an overflow reservoir of the slurry (Napier-Munn et al., DeBeers Diamond Research Laboratory, Johannesburg, 1985, in Kawatra and Eisele, loc. cit.). Vibrating and ultrasonic types can also be used.

A simple device [Montini and Moys, *J. South African Inst. Mining & Metallurgy,* **88**(6), 199–206 (1988)] measures slurry viscosity and hence percent solids within the mill. It consists of a bolt that passes through insulating washers in the shell. A measurement of electrical conduction is taken at a moment when the ball charge has just fallen away from the rotating shell. This measures the thickness of the slurry adhering to the vicinity of the bolt, which is related to the slurry viscosity. The device can distinguish among slurry concentrations of 60, 65, and 70 percent solids, and should be useful for computer control of viscosity in the mill.

Feed and Discharge Feed and discharge arrangements for ball and rod mills depend on their mode of operation. Various feed and discharge mechanisms are shown in Fig. 20-34.

Mill feeders attached to the feed trunnion of the conical mill and used to pass the feed into the mill without backspill are of several types. A feed chute is generally used for dry grinding, this consisting of an inclined chute which is sealed at the outer edge of the trunnion and down which the material slides to pass through the trunnion and into the mill. A screw feeder, consisting of a short section of screw conveyor which extends partway into the opening in the feed trunnion and conveys the material into the mill, may also be used when dry grinding. For wet grinding, several different types of feeders are available: the scoop feeder, which is attached to and rotates with the mill trunnion and which dips into a stationary box to pick up the material and pass it into the mill; a drum feeder attached to and rotating with the feed trunnion, having a central opening into which the material is fed and an internal deflector or lifter to pass the material through the trunnion into the mill; or a combination drum and scoop feeder, in which the new feed to the mill is fed through the central opening of the drum while the scoop picks up the oversize being returned from a classifier to a scoop box well below the centerline of the mill.

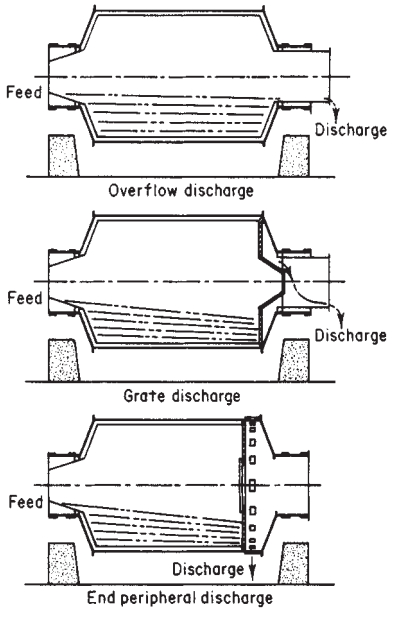


FIG. 20-34 Continuous ball-mill discharge arrangements for wet grinding.

Control of pulp level to obtain high-circulating load is accomplished by use of **grate-discharge mills.** In one case the grates allowed passage of sufficient pulp to maintain the circulating load at 400 percent (Duggan, *Min. Technol.,* Tech. Publ. 1456, March 1942).

Mill Efficiencies The controlling factors conceded to govern the ore-grinding efficiency of cylindrical mills are as follows:

1. Speed of mill affects capacity, also liner and ball wear, in direct proportion up to 65–75 percent of critical speed.
2. Ball charge equal to 35–50 percent of the mill volume gives the maximum capacity.
3. Minimum-size balls capable of grinding the feed give maximum efficiency.
4. Bar-type lifters are essential for smooth operation.
5. Material filling equal to ball-void volume is optimum.
6. Higher-circulating loads tend to increase production and decrease the amount of unwanted fine material.
7. Low-level or grate discharge with recycle from a classifier increases grinding capacity over the center or overflow discharge; but liner, grate, and media wear is higher.
8. Ratio of solids to liquids in the mill must be considered on the basis of slurry rheology.

Experimental evidence presented in a classic paper by Coghill and De Vaney ("Ball Mill Grinding," U.S. Bur. Mines Tech. Publ. 581, 1937) indicated that the efficiency of battered reject balls was about 11 percent less than that of new spherical balls. These and other results have been graphically presented (Rose and Sullivan, *Ball Rod and Tube Mills,* Chemical Publishing Co., NY, 1958).

Selection of Mill The selection of a ball- or rod-mill grinding unit is based on pilot-mill experiments, scaled up on the basis that production is proportional to energy input. When pilot experiments cannot be undertaken, performance is based on published data for similar types of materials, expressed in terms of either grindability or an energy requirement (see subsections "Grindability" and "Energy Laws"). Newer methods of sizing mills and determining operating conditions for optimum circuit performance are based on computer solutions of the grinding equations with values of rate and breakage functions determined from pilot or full-scale tests (see subsection "Simulation of Milling Circuits").

Capacity and Power Consumption One of the methods of mill sizing is based on the observation that the amount of grinding depends on the amount of energy expended, if one assumes comparable good practice of operation in each case. The energy applied to a ball mill is primarily determined by the size of mill and load of balls. Theoretical considerations show the net power to drive a ball mill to be proportional to $D^{2.5}$, but this exponent may be used without modification in comparing two mills only when operating conditions are identical [Gow, Guggenehim, Campbell, and Coghill, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **112,** 24 (1934)]. The net power to drive a ball mill was found to be

$$E = [(1.64L - 1)K + 1][(1.64D)^{2.5}E_2] \qquad (20\text{-}41)$$

where L is the inside length of the mill, m (ft); D is the mean inside diameter of the mill, m (ft); E_2 is the net power used by a 0.6- by 0.6-m (2- by 2-ft) laboratory mill under similar operating conditions; and K is 0.9 for mills less than 1.5 m (5 ft) long and 0.85 for mills over 1.5 m long. This formula may be used to scale up pilot-milling experiments in which the diameter and length of the mill are changed but the size of balls and the ball loading as a fraction of mill volume are unchanged. More accurate computer models are now available.

Morrell [*Trans. Instn. Min. Metall.,* Sect. C, **101,** 25–32 (1992)] established equations to predict power draft based on a model of the

shape of the rotating ball mass. Photographic observations from laboratory and plant-sized mills, including autogenous, semiautogenous and ball mills showed that the shape of the material charge could roughly be represented by angles that gave the position of the toe and shoulder of the charge. The power is determined by the angular speed and the torque to lift the balls. The resulting equations show that power increases rapidly with mill filling up to 35 percent, then varies little between 35 and 50 percent. Also, net power is related to mill diameter to an exponent less than 2.5. This agrees with Bond [*Brit. Chem. Engr.,* 378–385 (1960)] who stated from plant experience that power increases with diameter to the 2.3 exponent or more for larger mills. Power input increases faster than volume, which varies with diameter squared. The equations can be used to estimate holdup for control of autogenous mills.

The gross power drawn by the mill is the net power plus the power drawn by the empty mill due to friction of its weight on the bearings.

Motor and Drive The *ring motor* is a low-frequency synchronous motor with its windings mounted directly on the mill shell. Hamdani and Zarif (*Proc. IEEE Cement Industry Tech. Conference,* 32d, 57–80, 1990) compared ring-motor cement mills with geared mills. Although the ring motor has higher initial cost, the operating cost is lower. In particular the downtime for maintenance is lower; the availability based on 20 years experience is >99 percent, while it is 89 percent with geared drives. Ring motors were said to become economically favorable over gear drives at sizes above 8500 hp [Englund, *Power,* **125**(9), 111–2 (1981)].

Recent innovations [Knecht, *IEEE Transactions on Industry Applications,* **28**(4), 962–969 (1992)] have improved the cost effectiveness and reliability of geared-mill designs as well. Slide-shoe bearings support the ends of the mill body and eliminate alignment problems caused by strain on the ends, and allow more compact end design. The bearing pads can be adjusted to compensate for deviations of the slide ring or settlement of the foundation, better than trunnion bearings.

One major requirement of gears is checking and adjusting to close tolerance the alignment of the girth gear and pinion which drives it. To avoid much of this effort, a self-adjusting pinion has been developed which is mounted in tilting bearings. Another improvement is the mounting of tandem-pinion gears in a common housing with the bearing system (Combiflex drive, *Krupp Polysius AG*), which further reduces maintenance problems. Maintenance is also reduced by covering the ring gear and using a circulating oil-lubrication system, instead of manually-applied grease.

Girth-gear drives can cause the concrete foundations to fail if not designed to resist harmonic vibrations (Saxer and Van der Heuvel, 31st IEEE Cement Industry Conference, 1989).

Performance of Proprietary Equipment

Joy Denver Equipment Div Manufactures a variety of grinding mills. Designs incorporate cast steel heads, heavy rolled steel shell, replaceable cast steel trunnions, hydraulic starting lubricator, internally lubricated trunnion bearings, hard iron trunnion linings, heavy-duty spherical self-aligning anti-friction roller bearings, reversible forged and machined drive pinions, and split construction, reversible mill gears. Sole plates are adjustable. Drive types include V-belt, gear reducer with air clutch or direct, and drum, scoop, scoop-drum or spout feeders. Grinding media may be rod with overflow, end peripheral or center peripheral discharge, or balls with overflow or grate discharge.

Marcy Ball Mill (Fig. 20-31; *Mine and Smelter Div., Allis Mineral Processing Systems.*) This is traditionally a grate-discharge mill, used to give a high throughput rate for a high circulating load in the wet and dry grinding of ores. The data in Table 20-16 must not be used for design but for orientation only. Mill design must be based on pilot experiments or other techniques previously discussed.

Krupp Polysius AG Mineral Processing Systems Provides rod- and tube-ball mills from 0.6 to 6 m diameter and up to 15.7 m long. Structural analyses are by computer methods. The patented slide-shoe design compensates for journal deformation, and hardened-steel spherical pads allow the shoes to pivot. Lubrication oil is provided at high pressure for startup/shutdown, and low pressure for continuous running. Drive can be by single pinion to 5,200 kW, twin pinion to 4,500 kW or higher, or gearless from 6,700 kW. Mill linings may be cast Cr-Mo steel alloy, or alloys with Ni for abrasion resistance. Rubber linings are fitted for many wet-grinding processes.

Multicompartmented mills feature grinding of coarse feed to finished product in a single operation, wet or dry. The primary grinding compartment carries large grinding balls or rods; one or more secondary compartments carry smaller media for finer grinding.

STIRRED MEDIA MILLS

Applications overlap with those of vibratory mills, described in the next group. Vibrational equipment is generally used for hard-grinding operations ($ZrSiO_4$, SiO_2, TiO_2, Al_2O_3, etc.), while stirred grinders are mainly used for dispersion and soft grinding (dyes, clays, $CaCO_3$, biological cells, etc). Stirred mills are also called **sand mills** when Ottawa sand is used as media. Contamination and grinder-body wear may be minimized in both types by the use of resilient coatings. Stirred mills use media 6 mm (¼ in.) in size or smaller, whereas vibratory mills use larger media for the same power input. Vibratory mills may grind dry, but most stirred mills are restricted to wet milling. Solids vary from 25 to 70 percent, depending on the feed size and rheology. Unlike in rotary-ball mills, some sedimentation may occur. The media filling ranges from 60 to 90 percent of apparent filling of the mill volume.

Design In stirred mills, a central paddle wheel or disced armature stirs the media at speeds from 100 to 1500 r/min. The media oscillate in one or more planes and commonly rotate very slowly.

In the **Attritor** (*Union Process Inc.*) a single vertical armature rotates several long radial arms. These are available in batch, continuous, and circulation types. Morehouse-Cowles media mills comprise a

TABLE 20-16 Illustrative Performance of Marcy Ball Mills

Size, ft.	Ball charge, tons	Hp. to run	Mill speed, r.p.m.	Capacity, tons/24 hr. (based on medium-hard ore)								
				No. 8 sieve* 20% –200	No. 20 sieve 35% –200	No. 35 sieve 50% –200	No. 48 sieve 60% –200	No. 65 sieve 70% –200	No. 80 sieve 80% –200	No. 100 sieve 85% –200	No. 150 sieve 93% –200	No. 200 sieve 97% –200
3 × 2	0.85	5–7	35	19	15	12	10	8	6½	5	4	3
4 × 3	2.73	20–24	30	80	64	53	45	36	28	22	18	14
5 × 4	5.25	44–50	27	180	145	120	102	82	63	51	41	32
6 × 4½	8.90	85–95	24	375	300	250	210	170	135	105	85	66
7 × 5	13.10	135–150	22½	640	510	425	360	290	225	180	145	113
8 × 6	20.2	220–245	21	1100	885	735	625	500	390	310	250	195
9 × 7	30.0	345–380	20	1800	1450	1200	1020	815	635	505	410	315
10 × 10	56.50	700–750	18	3680	2960	2450	2100	1700	1325	1050	850	655
12 × 12	90.5	1260–1345	16.4	7125	5725	4750	4070	3290	2570	2035	1650	1275

*Sieve through which substantially all the material can pass.

NOTE: To convert horsepower to kilowatts, multiply by 0.746; to convert tons to megagrams, multiply by 0.907; and to convert tons per 24 hours to megagrams per day, multiply by 0.907.

vertical tubular chamber with coaxial rotating disks, and an integral variable-flow diaphragm pump. Models are available from 5 to 100 hp for aqueous and solvent slurries. The Netzsch LME4 mill can be operated with a feed rate up to 100 L/hr [Kula and Schuette, *Biotechnology Progress,* **3**(1), 31–42 (1987)].

Figure 20-35 illustrates the Drais continuous stirred-media mill. The media are stirred by discs mounted on a central shaft. The advantage of horizontal machines is the elimination of gravity segregation of the feed. The feed slurry is pumped in at one end and discharged at the other, where the media are retained by a screen or array of closely spaced flat discs. The latter is useful with slurries having viscosity up to 50 Pa·s (50,000 cP), while screens are useful up to 1 Pa·s. Hydrodynamically shaped screen cartridges can accommodate media as fine as 0.2 mm. German manufacturers [Stadler et al., *Chemie-Ingenieur-Technik,* **62**(11), 907–915 (1990)] have produced mills of various shapes, primarily to aid separation of beads from product. When the mill body rotates with the screen at the axis, centrifugal force aids this separation.

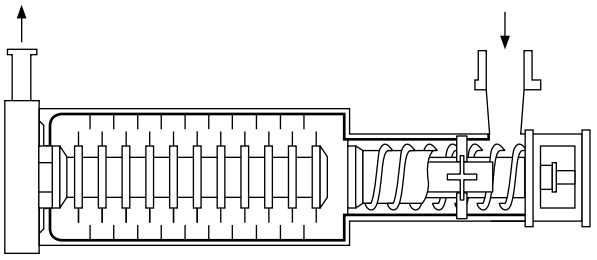


FIG. 20-35 Drais wet-grinding and dispersing system (U.S. patent 3,957,210) Draiswerke Gmbh. [*Stehr,* International J. Mineral Processing, ***22****(1–4), 431–444 (1988).*]

Agitator discs are available is several forms: smooth, perforated, eccentric, and pinned. Effect of disc design has received limited study, but pinned discs are usually reserved for highly viscous materials.

Cooling water is circulated through a jacket and sometimes through the central shaft. The working speed of disc tips ranges from 5 to 15 m/sec, regardless of mill size.

The continuously stirred mill can be fed by screw feeders from several material bins simultaneously, thus blending uniform compositions, without incurring problems of transporting imperfectly blended or agglomerated mixtures. A series of mills may be used with decreasing media size and increasing rotary speed to achieve desired fine-particle size. No additional feed pumps are needed.

The **annular gap mill** shown in Fig. 20-36 is a variation of the bead mill. It has a high-energy input as shown in Fig. 20-37. It may be lined with polyurethane and operated in multipass mode to narrow the residence-time distribution and to aid cooling.

Performance of Bead Mills Materials processed in stirred-media mills are listed in Table 20-17. Variables affecting the milling process are listed below.

Stirred bead-mill process variables:
Agitator speed
Feed rate
Size of beads
Bead charge, percent of mill volume
Cell concentration in feed
Density of beads
Temperature
Design of blades
Shape of mill chamber
Residence time

The availability of more powerful, continuous machines has extended the possible applications to both lower- and higher-size ranges, from 5 to 200 μm product size, and to feed size as large as 5 mm. The energy density may be 50 times larger than in tumbling-ball mills, so that a smaller mill is required (see Fig. 20-37). Mills range in size from 1 to 1000 L, with installed power up to 320 kW. Specific

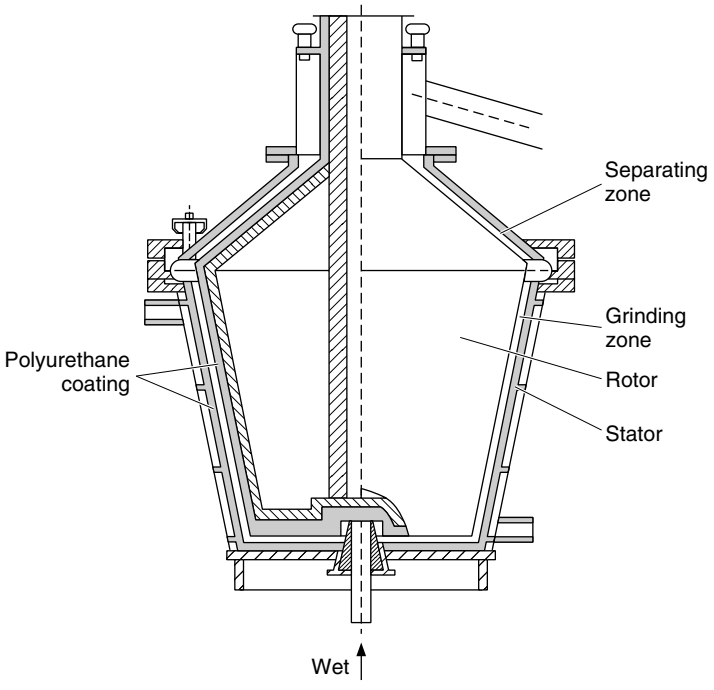


FIG. 20-36 Annular gap-bead mill (*Welte Mahltechnik, Gmbh.*) [*Kolb,* Ceramic Forum International, ***70****(5), 212–6 (1993)*].

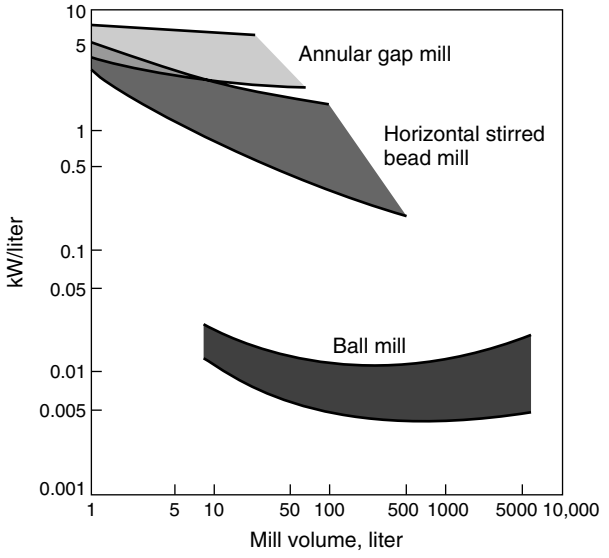


FIG. 20-37 Specific power of bead and ball mills [*Kolb,* Ceramic Forum International, ***70****(5), 212–6 (1993)*].

power ranges from 10 to 200 or even 2000 kWh/tonne, with feed rates usually less than 1 tonne/h. Required energy can be scaled-up using dimensionless numbers, as shown in Fig. 20-38.

The nature of the media can influence the grinding rate. Table 20-18 lists some currently used media. Steel balls were more effective in the fine grinding of coal than glass balls [Mankosa et al., *Powder Technology,* **49**(1), 75–82 (1986)], presumably because they have a higher density and greater impact energy than glass. There is also an optimum size of media, for coal about 20 times the size of the particle being ground. For large particles this appears to be related to the coefficient of friction which determines the nip angle. For small particles the capture zone is limited by the curvature of the bead, so that it is not feasible to reduce the size more than one order of magnitude with a given bead size. (For further examples see under Micas and Alumina.)

In vertical disc-stirred mills the media should be in a fluidized condition (White, *Media Milling,* Premier Mill Co., 1991). Particles can pack in the bottom if there is not enough stirring action or feed flow; or in the top if flow is too high. These conditions are usually detected by experiment.

A study of bead milling [Gao and Forssberg, *International J. Mineral Processing,* **32**(1–2), 45–59 (1993)] was done in a continuous Drais mill of 6 L capacity having seven 120 × 10 mm horizontal discs. Twenty-seven tests were done with variables at three levels. Dolomite was fed with 2 m^2/g surface area in a slurry ranging from 65 to 75 percent solids by weight, or 39.5 to 51.3 percent by volume. Surface area produced was found to increase linearly with grinding time or specific-energy consumption. The variables studied strongly affected milling rate; two extremes differed by a factor of 10. An optimum bead density for this feed material was 3.7. Evidently the discs of the chosen design could not effectively stir the more-dense beads. Higher slurry concentration above 70 wt % solids reduced the surface production per unit energy. The power input increased more than proportional to speed.

Residence Time Distribution Commercially available bead mills have a diameter-to-length ratio ranging from 1:2.5 to 1:3.5. The ratio is expected to affect the *residence time distribution* (RTD). A wide distribution results in overgrinding some feed and undergrinding another. Data from Kula and Schuette [*Biotechnology Progress,* **3**(1), 31–42 (1987)] shows that in a Netzsch LME20 mill RTD extends from 0.2 to 2.5 times the nominal time, indicating extensive stirring. (See "Cell Disruption" under Applications.) The RTD is even more important when the objective is to reduce the top size of the product as Stadler et al. [*Chemie-Ingenieur-Technik,* **62**(11), 907–915 (1990)] showed, because much of the feed received less than half the nominal residence time. A narrow RTD could be achieved by rapidly flowing material through the mill for as many as 10 passes.

TABLE 20-17 Materials Processed in Stirred-Media Mills (Stehr, *International J. Mineral Processing,* 22 1–4, 431–4, 1988).

Industry	Product
Paint & Lacquer	Primer coatings
	Lacquer
	Dispersion paints
Ink	Printing inks
	Dyestuffs
	Textile inks
	Pigment crudes activating
Chemical and pharmaceutical	Various
Electronics	High-grade ceramics
	Oxides for electric components
	Ferrites for permanent magnets
	Audio & Video coatings
Minerals	Limestone
	Fillers
	Paper coatings
	Flue gas desulfurization
	Kaolin
	Gypsum
	Alumina
	Precious metals liberation
Agrochemical	Pesticides
	Insecticides
	Herbicides
	Fungicides
Foods	Cocoa nibs
	Milk chocolate
	Peanuts
	Sesame
Biotechnology	Cell disruption
	Yeast disruption for enzyme extraction
Rubber	Dissolving polymers in solvents
Coal, energy	Coal-oil mixtures
	Coal-water slurry
	Gas turbine coal fuel
	Diesel coal fuel
	Fuel beneficiation, desulfurization

VIBRATORY MILLS

The dominant form of industrial vibratory mill is the type with two horizontal tubes, called the **horizontal tube mill.** These tubes are mounted on springs and given a circular vibration by rotation of a counterweight, shown in Fig. 20-39. Many feed flow arrangements are possible, adapting to various applications. Variations include polymer lining to prevent iron contamination, blending of several components, milling under inert gas and at high and low temperatures. An example is the Palla vibratory mill (*ABB Raymond Div, Combustion Engineering Inc.*).

The Vibro-Energy (*Sweco, Inc.*), a **vertical vibratory mill** (Fig. 20-40) has a mill body in a ring-shaped trough form but uses horizontal vibrations at a frequency of about 20 Hz of the contained media, usually alumina spheres or cylinders. Other characteristics appear in Table 20-19.

The vertical vibratory mill has good wear values and a low-noise output. It has an unfavorable residence-time distribution, since in continuous operation it behaves like a well-stirred vessel. Tube mills are better for continuous operation. The mill volume of the vertical mill cannot be arbitrarily scaled up because the static load of the upper media, especially with steel beads, prevents thorough energy introduction into the lower layers. Larger throughputs can therefore only be obtained by using more mill troughs, as in tube mills.

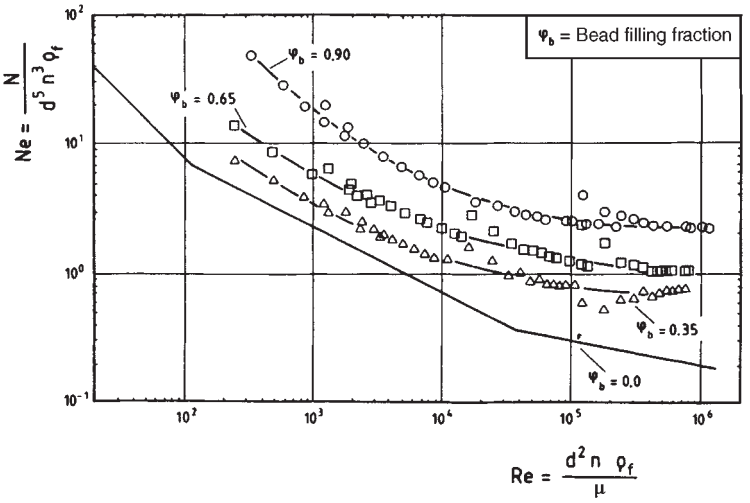


FIG. 20-38 Newton number as a function of Reynolds number for a horizontal stirred bead mill, with fluid alone and with various filling fractions of 1-mm glass beads [*Weit and Schwedes,* Chemical Engineering and Technology, ***10****(6), 398–404 (1987)*]. (*N* = power input, W; *d* = stirrer disk diameter, m; *n* = stirring speed, 1/s; μ = liquid viscosity, Pa·s; Q_f = feed rate, m^3/s.)

The primary applications of vibratory mills are in fine milling of medium to hard minerals primarily in dry form, producing particle sizes of 1 μm and finer. Throughputs are typically 10 to 20 t/hr. Grinding increases with residence time, active mill volume, the energy density and the vibration frequency, and media filling and feed charge. The amount of energy that can be applied limits the tube size to 600 mm, although one design reaches 1000 mm. Larger vibratory amplitudes are more favorable for comminution than higher frequency. The development of larger vibratory mills is unlikely in the near future because of excitation problems. This has led to the use of mills with as many as six grinding tubes.

Performance The grinding-media diameter should preferably be 10 times that of the feed and should not exceed 100 times the feed diameter. To obtain improved efficiency when reducing size by several orders of magnitude, several stages should be used with different media diameters. As fine grinding proceeds, rheological factors alter the charge ratio, and power requirements may increase.

A variety of grinding media are available, as shown in Table 20-18. Size availability varies, ranging from 1.3 cm (½ in) down to 325 mesh (44 μm).

Although there are no definitive data on media shape and grinding, ball-milling data indicate that spheres are the most effective shape. [Norris, *Trans. Inst. Min. Metall.,* **63**(567), 197–209 (1954)].

Although each machine has its peculiar characteristics and time requirements for various types of grinding, Fig. 20-40 illustrates some typical results obtained under optimum conditions for several materials.

Advantages of vibratory mills are (1) simple construction and low-capital cost, (2) very fine product size attainable with large reduction

TABLE 20-18 Media for Stirred and Vibratory Mills (* S = spheres, C = cylinders, I = irregular shapes)

Material	Common name	Density, g/cm³	Diameter, mm	Forms available*
Perfluoroethylene	Teflon	1.	—	C
Silicon dioxide	Ottawa sand	2.8	0.4–3.0	I
Annealed glass	Hard glass, unleaded	2.5	0.3–5.0	S
Annealed glass	Hard glass, leaded	2.9	0.3–5.0	S
Aluminum oxide	Alumina, Corundum	3.4	0.5–15.0	S,C,I
Zirconium silicate	Zircon	3.8	0.3–15.0	S,C,I
Zirconium oxide	Zirconia, Zircoa	5.4	0.5–3.0	S,C,I
Steel	Steel shot	7.6	0.2–15.0	S
Steel	Chrome steel	7.85	1.0–12.0	S

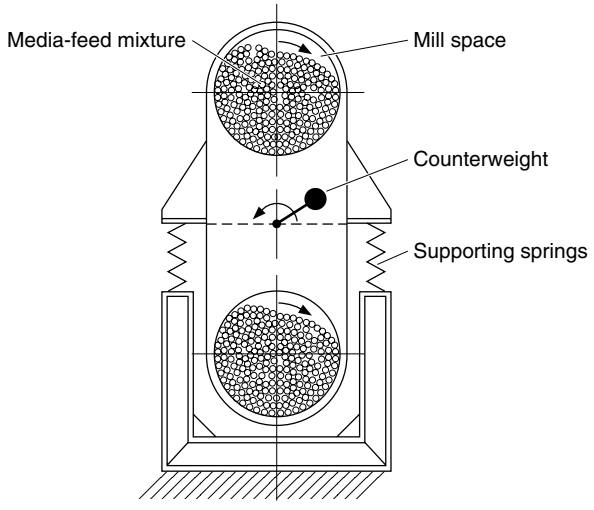


FIG. 20-39 Two-tube vibratory mill. (*Hoeffl,* Freiberger Forschungshefte A ***750,*** *125 pp., 1988.*)

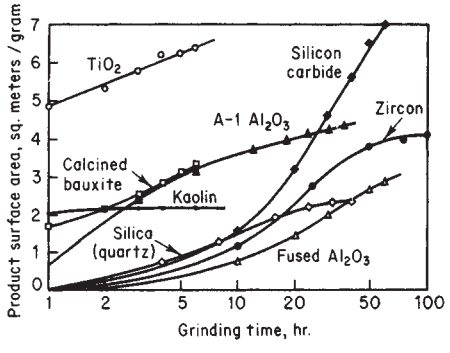


FIG. 20-40 Vibratory-mill typical performance. (*Sweco, Inc.*)

TABLE 20-19 Characteristics of Sweco Vibratory Mills

Designation	Capacity	Typical sample charge, lb	Motor	Mill diameter, in
M-18	2.6 gal	5–20	¼	18
M-45	20 gal	50–200	5	45
M-60	70 gal	200–1000	10	60
M-80	182 gal	500–2000	40	80
DM-1	0.125 ft^3	3–5	⅓	24
DM-3	0.5 ft^3	20–60	1¼	30
DM-10	3 ft^3	100–400	5	45
DM-20	65 ft^3	200–800	10	60
DM-70	23 ft^3	900–3000	40	95

NOTE: To convert gallons to cubic meters, multiply by 3.785×10^{-3}; to convert pounds to kilograms, multiply by 0.4535; to convert horsepower to kilowatts, multiply by 0.746; and to convert inches to centimeters, multiply by 2.54.

ratio in a single pass, (3) good adaptation to many uses (4) Small space and weight requirements, (5) ease and low cost of maintenance. Disadvantages are (1) limited mill size and throughput, (2) vibration of the support and foundation, (3) high-noise output, especially when run dry.

Residence Time Distribution Hoeffl (Freiberger *Forschungshefte A,* **750,** 119 pp., 1988) carried out the first investigations of residence time distribution and grinding on vibratory mills, and derived differential equations describing the motion. In vibratory horizontal-tube mills the mean axial transport velocity increases with increasing vibrational velocity, defined as the product $r_s\Omega$, where r_s = amplitude and Ω = frequency. Apparently the media act as a filter for the feed particles, and are opened by vibrations. Nevertheless, good uniformity of transport is obtained, indicated by *vessel dispersion numbers* $D\tau/L^2$ (see "Simulation of Milling Circuits" above) in the range 0.06 to 0.08 measured in limestone grinding under conditions where both throughput and vibrational acceleration are optimum.

The vibratory-tube mill is also suited to wet milling. In fine wet milling this narrow residence time distribution lends itself to a simple open circuit with a small throughput. But for tasks of grinding to colloid-size range, the stirred media mill has the advantage.

NOVEL MEDIA MILLS

Planetary Ball Milling This is a method of increasing the gravitational force acting on balls in a ball mill. For example, refractory metals and carbides can be ground to 1 to 2.6 μm in 5 to 20 min in an apparatus capable of applying a centrifugal force of 10 to 50 G. [Dobrovol'skii, *Poroshk. Metall.,* **7**(6), 1–7 (1967)].

Pulverit planetary mills are available from Geoscience Inc. High-speed planetary-ball mills can be used to perform rapid tests to simulate ball milling of materials [Vock, *DECHEMA-Monogr.,* **69,** III-8 (1972)]. The size of high-speed mills will be much smaller than the size of same-capacity ball mills [Bradley, *S. Afr. Mech. Eng.,* **22,** 129 (1972)].

PARTICLE-SIZE CLASSIFIERS USED WITH GRINDING MILLS

Ball mills or tube mills can be operated in closed circuit with external air classifiers with or without air sweeping being employed. If air sweeping is employed, a cyclone separator may be placed between mill and classifier. (The principles of size reduction combined with size classification are discussed under "Characteristics of Size Classifiers.") Likewise other types of grinding mill can be operated in closed circuit with external size classifiers (Fig. 20-12), as will be described at appropriate places on succeeding pages. However, many types of grinders are air-swept and are so closely coupled with their classifiers that the latter are termed internal classifiers.

Dry Classifiers Dry **screens** are used primarily in crusher circuits, since they are most effective down to 4 mesh. They can sometimes be used to 35 mesh. Examples are *Hummer* screens (*W. S. Tyler, Inc.*), *Rotex* screens (*Rotex Inc.*), and the *Vibro-Energy separator* (*Sweco, Inc.*).

Most dry-milling circuits use **air classifiers.** There are a number of types, but all use the principles of air drag and particle inertia, which depend on particle size. The simplest type of air classifier is an elutriator. A countercurrent multielement elutriator is the Zig-Zag classifier (*Hosokawa Micron Powder Systems Div.*). The sharpness of separation increases with the number of elements. These devices are effective in the 30- to 80-mesh range.

Another type of classifier directs an air stream across a stream of the particles to be classified. An example is the radial-flow classifier (*Kennedy Van Saun Corp.*), which features adjustable elements to control the flow and classification. A further development on this principle is the Vari-Mesh classifier (*Kennedy Van Saun Corp.*), which controls classification by adjustable flow baffles. A change in direction of air flow is the operating principle of the reverse-flow Superfine classifier (*Hosokawa Mineral Processing Systems*).

Rotating blades are the main elements of several types of classifiers. The blades set up a centrifugal motion that tends to throw coarser particles outward. An example is the Mikro-ACM Pulverizer, in which an external fan forces air inwardly through the blades, carrying with it the fines. Centrifugal motion returns coarse particles to the hammers. The whizzer blades shown on the Raymond vertical mill (Fig. 20-49) have a similar centrifugal effect, throwing coarse particles to the wall of the chamber, where the lower boundary-layer air velocity allows them to fall back to the grinding zone.

Rotor blades also form an element of several external classifiers that are used in closed-circuit dry milling. These are generally called mechanical air separators or classifiers. Examples are the Whirlwind classifier (*Sturtevant Inc.*), the Gayco centrifugal separator (*Universal Road Machinery Co.* (see Fig. 20-41), and the whizzer separator (*Raymond Division of Combustion Engineering Inc.*).

Some mechanical air classifiers are designed so that the fine product must pass radially inward through rotor blades instead of spirally moving across them as with whizzer blades. Examples are the Mikron separator (*Hosokawa Micron Powder Systems Div.*), Sturtevant Side Draft separator, and the Majac classifier shown attached to the Majac jet mill (Fig. 20-55).

There are several mechanical air classifiers designed to operate in the superfine 10- to 90-μm range. Two of these are the Mikroplex spiral air classifier MPVI (*Hosokawa Micron Powder Systems Div.*) and the classifier which is an intregal part of the Hurricane pulverizer-classifier (*ABB Raymond Div, Combustion Engineering Inc.*) described under "Hammer Mills." Others are the Majac classifier (*Hosokawa Micron Powder Systems Div.*), the Sturtevant Superfine Air Separator, and the Bradley RMC classifier. These also use a vaned rotor, but operate at higher speed with higher power input and lower throughput.

Performance Deflector-type classifiers without rotating elements may give a product 85 percent through a 250-μm sieve, although more typically they give a product 95 percent below 74 μm. Mechanical air classifiers with rotating elements can give a product from 85 percent through 250 μm to as fine as 99.9 percent below 44 μm. The single whizzer is designed for operation where finenesses range to about 95 percent passing 74 μm, whereas the double-whizzer separator is intended for use where higher-fineness products, in the range of 99.9 percent or better passing 44 μm, are required. Sizes of mechanical air classifiers range from 1 to 7 m (3 to 24 ft) in diameter, with power requirements from 2 to 450 kW (3 to 600 hp). Superfine types can give a product 98 percent through 10 μm.

Typical separation efficiency curves of an air classifier versus particle size are given in Fig. 20-14. The amount of top size in the fines may be very low, but there is typically 10 to 30 percent fines in the coarse product; that is, the low end of the curve tends to flatten out at 10 to 30 percent. In addition, the separation at the cut size is typically a gradual curve. Data of this sort, which are needed to evaluate closed-circuit mill performance, are seldom available. See subsection on characteristics of size classifiers for a testing method.

The Sturtevant air separator (*Sturtevant Inc.*) incorporates a hydraulic mechanism to adjust the width of the ring baffle over the spinner blades, which allows adjusting the separation curve within limits, at some cost in production rate. For example, the residue on 74-μm screen can be varied from 1 to 20 percent, with a production rate shown in Table 20-20 for cement rock.

An improved version of the Raymond classifier sends all the air to the product-collector cyclone, returning only solids. This improves

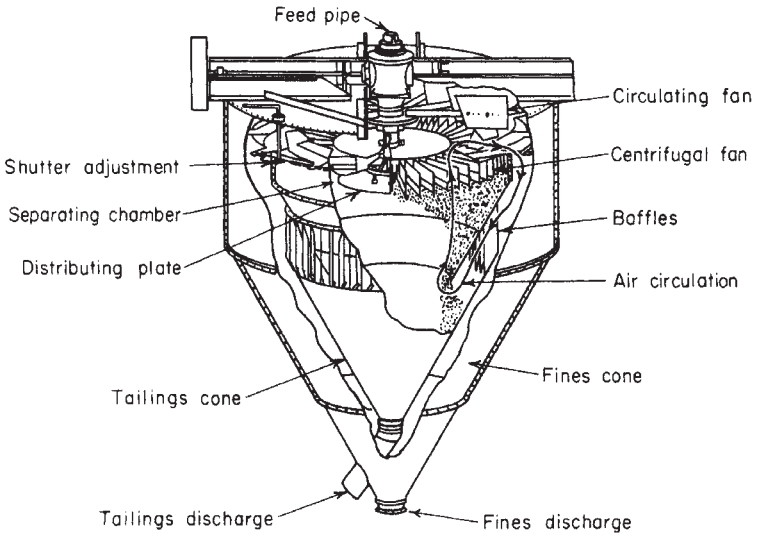


FIG. 20-41 Typical centrifugal separator.

fines production, since air returned with coarse material otherwise carries fines.

Wet Classifiers Closed-circuit wet milling is the rule in large-scale operations because of its greater production and economy. The simplest wet classifier is a **settling basin** arranged so that the fines do not have time to settle but are drawn off while the thickened coarse product is raked to a central discharge. Examples are the Hardinge Hydro-Classifier and the Dorr thickener. For classification near micrometer size a **continuous centrifuge** such as the Sharpless supercentrifuge or the Bird centrifuge is effective. The separation is not sharp in settlers, and the large space requirement is a detraction. **Rake classifiers** and **screw classifiers** are described in Sec. 21. The action is countercurrent, so separation of coarse grains is more effective. Examples are the Hardinge countercurrent (screw) classifier (Fig. 20-42) and the Dorr-Oliver rake classifier (Fig. 20-43). Typical circuits used with these classifiers in cement- and ore-processing plants are shown in Figs. 20-43 and 20-44. **Hydrocyclones** have become the most popular wet classifiers in ore operations owing to their compact design and economy of operation. Control is effected by feeding at a constant rate from a sump, in which the liquid level is maintained by varying water addition as the slurry feed rate varies (see Fig. 20-45).

In the 1930s there were attempts to use **screens** for wet closed-circuit milling, but operating cost was prohibitive. Recently screens have been developed that are practical for mill circuits. The first of these was the Dutch State Mines screen, which has the screen cloth on a curved incline, with the dilute slurry flowing over and through it. Because of the angle of attack, the effective opening is smaller than the physical opening, so blinding does not occur, but the separation is less sharp.

The use of rubber screen cloths also solves problems of blinding [Wessel, *Aufbereit. Tech.*, **8**(2), 53–62; (5), 167–80; (8), 417–428 (1967);

TABLE 20-20 Production Rate of Sturtevant Air Separator at 74 μm

Separator diameter		Fines production	
m	ft	Mg/h	ton/h
0.9	3	0.4–1.0	0.4–1.1
2.5	8	3–9	3–10
4.3	14	15–40	17–45
6.1	20	77–210	85–230
8.0	26	180–450	200–500

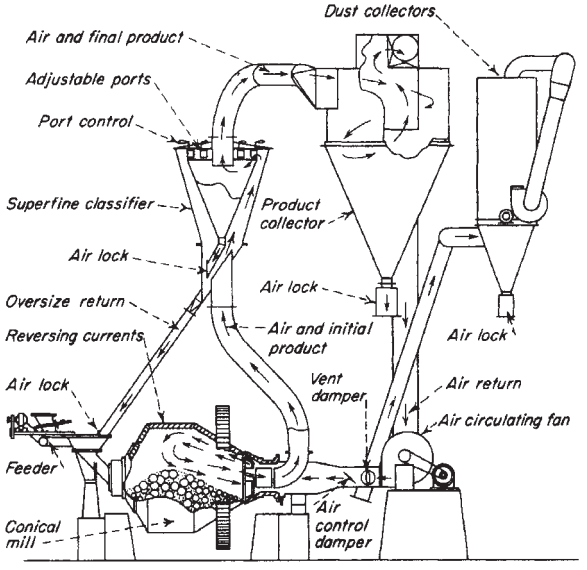


FIG. 20-42 Hardinge conical mill with reversed-current air classifier.

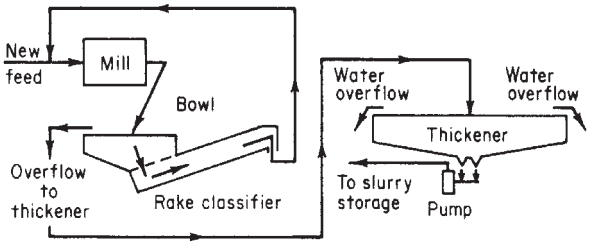


FIG. 20-43 Single-stage closed-circuit wet-grinding system. [*Tonry,* Pit Quarry (*February–March 1959*).]

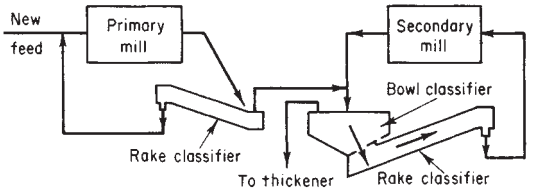


FIG. 20-44 Two-stage closed-circuit wet-grinding system. [*Tonry,* Pit Quarry (*February–March 1959*).]

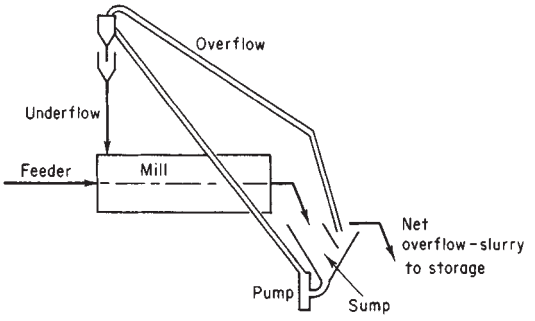


FIG. 20-45 Closed-circuit wet grinding with liquid-solid cyclone. [*Tonry,* Pit Quarry (*February–March 1959*).]

Michel, *Min. Mag.* (*London*), annual review issue (5), 189–193, 207 (1968)]. An upper layer of rubber is perforated with fine slots for particle sizes from 0.2 to 2.5 mm., and this is supported by a lower layer with coarse holes. The vibration rate is 2500 to 3000 cycles/min. The advantage of screens over other classifiers is that a considerably sharper separation can be effected, and less fines are returned to the mill. Screen separation is considerably less than perfect, although there are few published data. The selectivity of a screen depends on the screen opening size and the feed rate, as well as other variables. A semiempirical model for an inclined vibratory screen [Karra, *CIM Bulletin,* 167–171 (Apr. 1979); *Proc. 14th International Mining Congress,* Toronto, **III**(6), 1–614; King, *International J. Mineral Processing,* **29**(3–4), 249–265 (1990)] includes factors for these effects.

HAMMER MILLS

Hammer mills for fine pulverizing and disintegration are operated at high speeds. The rotor shaft may be vertical or horizontal, generally the latter. The shaft carries hammers, sometimes called beaters. The hammers may be T-shaped elements, stirrups, bars, or rings fixed or pivoted to the shaft or to disks fixed to the shaft. The grinding action results from **impact** and **attrition** between lumps or particles of the material being ground, the housing, and the grinding elements. A cylindrical screen or grating usually encloses all or part of the rotor. The fineness of product can be regulated by changing rotor speed, feed rate, or clearance between hammers and grinding plates, as well as by changing the number and type of hammers used and the size of discharge openings.

The **screen** or **grating discharge** for a hammer mill serves as an internal classifier, but its limited area does not permit effective usage when small apertures are required. A larger external screen may then be required.

The feed must be nonabrasive with a hardness of 1.5 or less. The mill is capable of taking 2-cm (¾-in) feed material, depending on the size of the feed throat, and reducing it to a product substantially all able to pass a No. 200 sieve. For producing materials in the fine-size range, it may be operated in conjunction with external air classifiers. Such an arrangement is shown in Figs. 20-12 or 20-42. A number of machines have internal air classifiers.

Hammer Mills without Internal Air Classifiers The **Mikro-Pulverizer** (Fig. 20-46) (*Hosokawa Micron Powder Systems Div.*) is a close-clearance, screen discharge, high-speed, controlled sealed-feed hammer mill used for a wide range of nonabrasive materials, the major applications being sugar, carbon black, chemicals, pharmaceuticals, plastics, dyestuffs, dry colors, and cosmetics. For performance see Table 20-21. Speeds, types of hammers, feed devices, housing variations, and perforations of screens are all varied to fit applications, with the result that finenesses and character of grind cover a wide range. Some of the grinds are as fine as 99.9 percent through a 325-mesh screen. Feed material should usually be down to 4 cm (1½ in) or finer. If feed is larger, an auxiliary crusher may be required, preferably as a separate unit, because synchronization is difficult since the crusher has larger capacities than the pulverizer. Tie-in is possible with careful regulation of relative speeds of crusher and feed screw or screws.

A replaceable liner for the mill housing cover is made with multiple serrations. Hammer tips can be provided with tungsten carbide inserts for greatest wear resistance or with Hastellite tipping. An air-injector feeder can be supplied to project the feed particles directly in front of the hammer tips, to provide a more direct blow and thus increase mill efficiency. Cinematographic studies show that otherwise the particles receive a glancing blow from hammers. Wet feed can be charged with feed screws or pumps for wet grinding. Mikro-Pulverizers are made in five sizes shown in Table 20-21, plus a 150-hp size. The smallest size is the Bantam, which is widely used in laboratories for development and pilot work. Results will indicate in a qualitative way what may be expected of full-scale production units.

The **Imp pulverizer** (*Raymond Division, Combustion Engineering Inc.*) is an air-swept hammer mill. This machine is made in many sizes from the smallest, using 18 kW (25 hp), to the largest size, with six rows of hammers and requiring 700 kW (1000 hp) to drive it. The machines are equipped with a hopper below which is the star feeder, actuated by a pawl-and-ratchet mechanism. The Imp mill is generally used as part of an air-swept classifying circuit such as shown in Fig. 20-42. Any type of classifier can be used, depending on the application. Any solid material with a top size of 1 in. that is softer than 2 on the Moh scale can be processed to a fineness ranging from 1000 to 45 μm.

The **Blue Streak dual-screen pulverizer** (*Prater Industries, Inc.*) is used for the grinding of resins, chemical salts, plastic scrap, food products, and similar materials to a granular uniform powder of No. 30 or No. 40 sieve fineness. Feed enters opposite ends of the rotor and undergoes three stages of size reduction by hammers of decreasing size. Two perforated screens cover more than 70 percent of the area of the final sizing drum through which the product passes.

The **Atrita pulverizer** (*Riley Stoker Corp.*) is available in several single and duplex types. Capacities vary from 3400 to 25,000 kg/h (7500 to 54,000 lb/h). The coal is carried in a a pin mill where most of the pulverizing is done, followed by a recycling classifier.

Hot air can be introduced into the machine for drying the coal. Air at 150°C dries coal with 8 percent moisture down to about 1 percent.

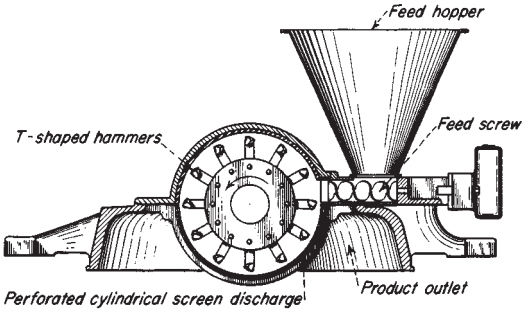


FIG. 20-46 Mikro-Pulverizer hammer mill. (*Hosokawa Micron Powder Systems Div.*)

TABLE 20-21 Mikro-Pulverizer Performance

Size	Rotor diam., in.	Max. r.p.m.	Hp.	Avg. capacities, lb./hr.		
				6X sugar	Clay-graphite water slurry	Pigments and colors (dry)
Bantam	5	16,000	¾–1	75–100	75–100	70–90
1	8	9,600	3–5	350–550	550	300–500
2	12	6,900	7½–15	800–1500	750–1600	800–2000
3	18	4,600	20–40	2000–4500	4500	2500–4500
4	24	3,450	40–100	4000–9000	7000	4500–7000

NOTE: To convert inches to centimeters, multiply by 2.54; to convert horsepower to kilowatts, multiply by 0.746; and to convert pounds per hour to kilograms per hour, multiply by 0.4535.

The **Aero pulverizer** (*Foster Wheeler Corp.*) is used for coal, pitch, and coke, blowing the ground material directly into the furnace. The housing is divided into two or three short cylindrical pulverizing chambers.

Hot gases can be introduced to dry the fuel being pulverized. Refractory material such as tramp iron is removed in the first pulverizing chamber and eliminated through a tramp-iron pocket.

Disintegrator The Rietz machine (Fig. 20-47) consists of a rotor running inside a 360° screen enclosure. The rotor includes a number of hammers designed to run at fairly close clearance relative to the inside of the cylindrical screen enclosing the disintegration chamber. The hammers are normally fixed rigidly to the shaft by keyways, pins, or welding, but swing hammers are used when indicated.

Rietz disintegrators are supplied in three types. *In-line disintegrators* (RI series) are designed for in-line installation, in which they function without impeding the process flow. Their primary applications are the mixing, delumping, and dissolving of fluids, slurries, and pastes and the grinding and separation of high-fiber solids.

Angle disintegrators (RA and RP series) are used for the fine pulping of many food products and for fine dispersion and homogenizing in the food and chemical industries. *Vertical disintegrators* (RD series) are used for dry pulverizing, wet grinding to produce slurries or pastes, shredding, defibrizing, and the fine pulping of soft fruits and vegetables.

Rietz disintegrators are normally supplied in rotor diameters from 10 to 60 cm (4 to 24 in), with rotational speeds to produce hammer tip speeds in ranges of 300 to 6700 m/min (1000 to 22,000 ft/min) and power ranges from 0.4 to 150 kW (½ to 200 hp). Higher speeds and higher power are available. AC variable-frequency drives can eliminate belts and provide easier variation of speed. Models are available in various materials of construction and in highly sanitary, easy-cleaning models or heavy-duty industrial construction (Table 20-22).

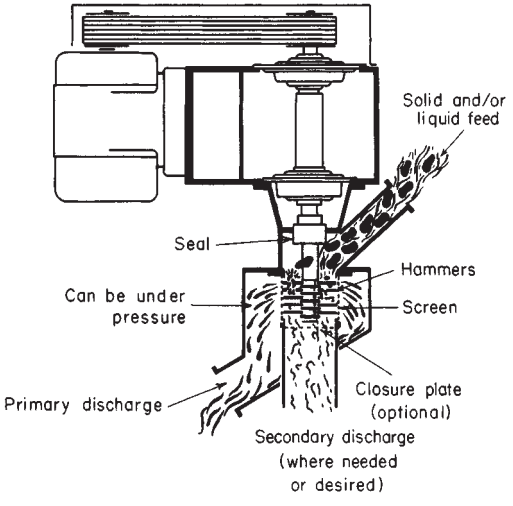


FIG. 20-47 Rietz disintegrator. (*Rietz Div. Hosokawa Bepex Corp.*)

Fitz mills (*Fitzpatrick Co.*) consist of several series of hammer mills in configurations adapted to a variety of uses in food processing. There are high-speed screen hammer mills with flat hammers for impact, and narrow hammers or sharp hammers for tough plastic or fibrous materials. There are long, small-diameter rotating mills for processing pastes and two-shaft toothed masticators. There are also single-roll toothed choppers and shredders with fixed knives.

Prater Industries, Inc., manufactures narrow swing-hammer screened mills for oilseeds and fibrous materials.

Turbo pulverizers and **turbo mills** (*Pallmann Pulverizer Co.*) combine the action of hammer and attrition mills, finding special application for grinding plastic materials that would be softened under high-energy warm-mill conditions.

Pin Mills In contrast to peripheral hammers of the rigid or swing types, there is a class of high-speed mills having pin breakers in the grinding circuit. These may be on a rotor with stator pins between circular rows of pins on the rotor disk, or they may be on rotors operating in opposite directions, thereby securing an increased differential of speed. See also the Mikro-ACM pulverizer described later.

Fine impact mills (*Hosokawa Micron Powder Systems Div.*) are high-speed impact mills with one stationary and one rotating stud disk. The mills are operated without a sieve and hence can be used with materials that tend to block (see Fig. 20-48). The **Contraplex wide chamber** is a similar mill with both disks rotating. It is suitable for grinding materials that tend to form deposits or for greasy, heat-sensitive products. These mills are used in the grinding of food, pesticides, pigments, and soft minerals, the wet grinding of PVC suspensions, and the crushing of cacao beans, etc. A laboratory model is also available.

Entoleter impact mills (*Entoleter, Inc.*) and the **Simpactor impact Mill** (*Sturtevant Inc.*) are a class of vertical-shaft devices in which feed at the shaft is caused to move rotationally and is thrown outward from the rotor to impact on an outer ring. Pin-type structures have been found effective; and in these the pins on the rotor do primary breakage, while the outer ring of pins gives further reduction. A wide range of speeds is employed, the higher ones being used for fine pulverizing. These mills grind a great variety of free-flowing or semi-free-flowing substances. Among these are plastics, rubber, grain and flour, coal, clay, slag, and salts. In some cases, external classification is required to remove oversize for return to the mill, or the mill may be combined with a classifier that contains no driven elements. Plastic materials are embrittled by liquid nitrogen or other suitable refrigerants to reduce their elasticity. For the highest speeds, the stator pins are mounted on a ring which is moving in reverse rotation to the central rotor.

Hammer Mills with Internal Air Classifiers The rotating components of the Raymond **vertical mill** are carried on its vertical shaft. They are the grinding element, double-whizzer classifier, and fan, as shown in Fig. 20-49. This mill has a hammer-tip speed of 7600 m/min (25,000 ft/min), so that it is effective for finer grinding than the Imp mill, which has a tip speed of 6400 m/min (21,000 ft/min).

The fine product is carried in the air stream through the fan and discharge port and separated by a cyclone collector into a suitable container.

Machines are available with rotor diameters of 45.7 and 88.9 cm (18 and 35 in), driven by 15- and 110-kW (20- and 150-hp) motors respectively. The larger mill is directly connected to a vertical motor. Normal rotor speed for the 45.7-cm (18-in) Raymond vertical mill is 6000 r/min and 3600 r/min for the 88.9-cm (35-in) machine.

The field of application of the Raymond vertical mill is the production of soft materials that range in size from those having 99 percent passing a 44-μm sieve to those having 99 percent smaller than 15 μm, depending on the state of aggregation of the feed. A production rate of 227 kg/h (500 lb/h) is achieved with a chemical in a 45.7-cm (18-in) machine, consuming 13.4 kW (18 hp) when the product is substantially smaller than 15 μm. In a talc operation on a 88.9-cm (35-in) machine requiring 110 kW (150 hp), a production rate of 320 kg/h (700 lb/h) is obtained. At a production rate of 2250 kg/h (5000 lb/h), a sample of the product leaves only a trace of talc on a No. 325 testing sieve.

TABLE 20-22 Performance of Rietz Disintegrators

Model	Rotor diam., in.	Max. r.p.m.	Hp. range	Screen perforation, in.	Typical applications	
					Material	Capacity
RA-1	4	16,000	½–5	1/32–¼	General lab use	1–10 lb./min.
RP-6	6	3,600	1–20	3/16	Horseradish	300 lb./hr.
RI-2	6 or 8	5,000	3–20	1/16	Detergent delumping	100 gal./min.
RD-8	8	8,400	3–20	⅛	Color coat	3600 lb./hr.
RA-2	8 or 12	8,400	3–20	1/32	Meat, cooked	3000–5000 lb./hr.
RP-8	8	3,600	10–60	¼	Blood declotting	20 gal./min.
RD-12	12	7,200	15–50	¼–¾	Polystyrene	3000–10,000 lb./hr.
RA-3	12 or 18	6,500	10–75	3/64	Corn, heated	350 lb./min.
RP-12	12	3,600	20–75	⅜	Asbestos-cement slurry	200 gal./min.
RD-18	18	3,600	30–150	⅜	Chemical-fertilizer delumping	15 tons/hr.
RP-18	18	3,600	25–100	¼	Animal fat (90°F.)	15,000 lb./hr.
RD-24	24	3,600	75–400	1	Wood-chip shredding	30 tons/hr.
RI-4	24	3,600	50–200	¼	Bagasse depithing	30 tons/hr. (dry)

Maximum horsepower depends upon maximum speed.
RA and RP models are normally supplied with stainless-steel contact parts.
Some disintegrators are available for operation under pressure.
Screens are available in various sizes and types of perforations down to 0.006 in.
NOTE: To convert inches to centimeters, multiply by 2.54; to convert horsepower to kilowatts, multiply by 0.746; and to convert pounds per hour to kilograms per hour, multiply by 0.4535.

The **Mikro-ACM pulverizer** is a pin mill with the feed being carried through the rotating pins and recycled through an attached vane classifier. The classifier rotor is separately driven through a speed control which may be adjusted independently of the pin-rotor speed. Oversize particles are carried downward by the internal circulating air stream and are returned to the pin rotor for further reduction. The constant flow of air through the ACM maintains a reasonable low temperature which makes it ideal for handling heat-sensitive materials. Typical capacities are given in Table 20-23. The mill is built in eight sizes: model 2 to model 400 with drive motor from 5 to 400 hp and production rates from 0.2 to 36 times the rate in Table 20-26.

The **Pulvocron** (*Hosokawa Bepex Corp.*) employs one or more beater plates, around the periphery of which are attached rigid hammers of hard metal. It is driven within a casing at clearances of small fractions of an inch, the periphery of which is generally V-cut. The grinding ring has provision for cooling with liquid in direct contact with its periphery. Feed enters around the driving shaft and is broken by breaker plates. It then travels to a classifying chamber, in which is a separately driven and controlled rotor with vanes. See Table 20-24.

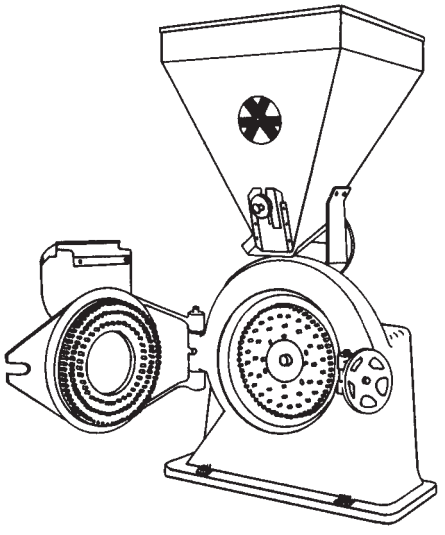


FIG. 20-48 Fine-impact mill. (*Hosokawa Micron Powder Systems Div.*)

RING-ROLLER MILLS

Ring-roller mills (Fig. 20-50) are equipped with rollers that operate against grinding rings. Pressure may be applied with heavy springs or by centrifugal force of the rollers against the ring. Either the ring or the rollers may be stationary. The grinding ring may be in a vertical

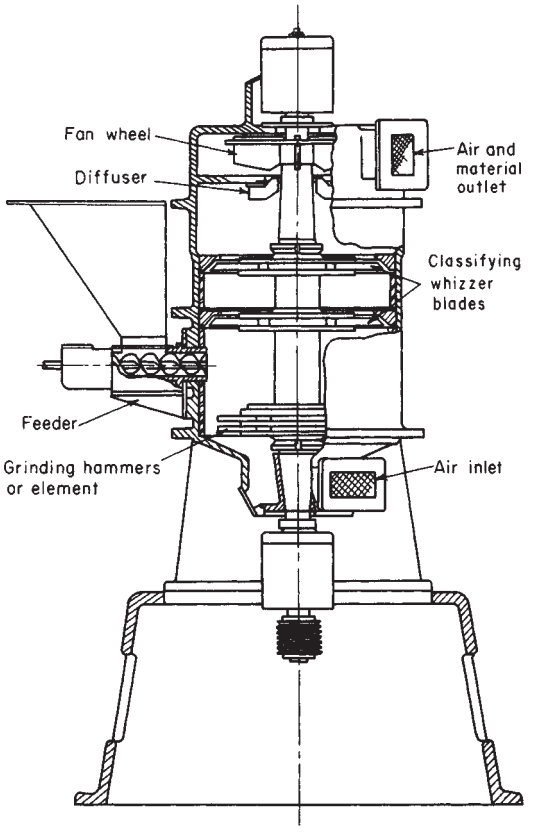


FIG. 20-49 Raymond vertical mill. (*Raymond Division, Combustion Engineering Inc.*)

TABLE 20-23 Test Results on Model 10 Mikro-ACM Pulverizer

Material	Fineness, d97, μm		Output, lb/h
	Feed	Product	
Alumina	45	11	519
Calcined coke	3000	79	315
Clay	850	45	750
Cocoa/sugar	300	44	100
Corn starch	105	62	300
Dextrose	1200	75	700
Diatomaceous earth	70	35	800
Graphite	150	45	250
Herbicide	150	45	790
Kaolin	200	9.6	600
Limestone	6000	45	360
Phenolic resin	9000	75	1140
Starch	25000	180	400
Sugar	450	75	1000
Sugar	450	30	850
Talc	43	12	80
Titanium dioxide	6000	30	1000
Wood flour	2000	125	40
Xanthan gum	6000	180	70

NOTE: 100 mesh = 150 μm; 200 mesh = 75 μm; 325 mesh = 45 μm

TABLE 20-24 Performance of the 20-in Pulvocron

Material	Particle analysis, by weight	Capacity, lb./hr.	Hp.
Sucrose	97.5% minus 325 mesh	1800	60
Sodium chloride	99.4% minus 100 mesh	3600	50
	99.95% minus 325 mesh	160	45
Urea-formaldehyde and melamine molding compounds	99.2% minus 80 mesh	1600	45
Paraformaldehyde	99.7% minus 325 mesh	1300	40
Casein	99% minus 80 mesh	650	50
Corn flour	88% minus 200 mesh	800	35
Soy flakes	95% minus 200 mesh	2000	60
Sterols	100% minus 5 μ	700	60
Lactose	98.5% minus 200 mesh	1200	40
Alumina, hydrated	99% minus 325 mesh	700	30
Cinnamon	99.7% minus 60 mesh	1000	50

NOTE: To convert pounds per hour to kilograms per hour, multiply by 0.4535; to convert horsepower to kilowatts, multiply by 0.746.

or a horizontal position. Ring-roller mills also are referred to as ring-roll mills or roller mills or medium-speed mills. The ball-and-ring and bowl mills are types of ring-roller mill.

Ring-roller mills are more energy efficient than ball mills or hammer mills. The energy to grind coal to 80 percent passing 200 mesh was determined (Luckie and Austin, *Coal Grinding Technology—A Manual for Process Engineers*) as: ball mill—13 hp/ton; hammer mill—22 hp/ton; roller mill—9 hp/ton.

Ring-roller mills should be distinguished from roller mills. Paint roll mills are described under "Disk Attrition Mills," and flour roll mills under "Cereals and Other Vegetable Products."

Ring-Roller Mills without Internal Classification Known examples are no longer produced.

Ring Mills with Internal Screen Classification The grinding action of the Hercules (*Bradley Pulverizer Co.*) is that of three rolls that are revolved around and against a die to create grinding pressures of approximately 100 MPa (15,000 lbf/in^2). It can produce minus-20-mesh agricultural limestone or phosphate rock from minus-5-cm (–2-in) feed. The material is discharged from the grinding chamber through a surrounding screen. Capacity is relatively high, being 23 to 45 Mg/h (25 to 50 tons/h) of average-hardness dry limestone. Other product sizes may be obtained by changing the screen aperture.

The B & W pulverizer, Type E, consists of a single row of balls operating between a rotating bottom ring and a stationary top ring. Externally adjusted springs apply pressure to the top ring to give the required loading for proper pulverizing. In operation wet raw coal is

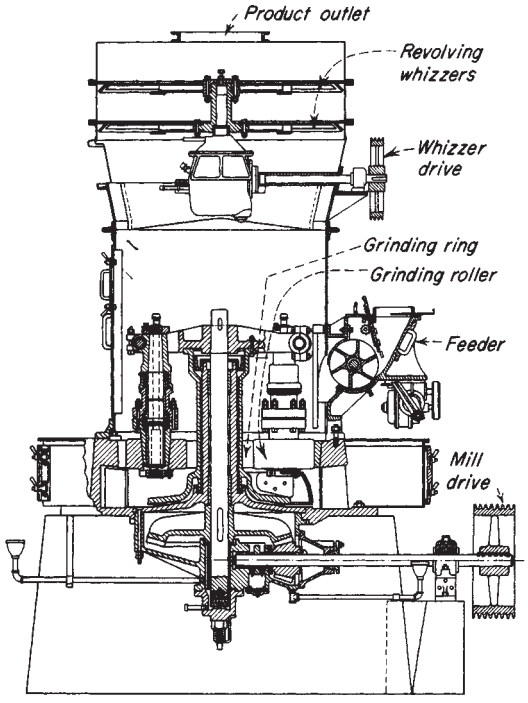


FIG. 20-50 Raymond high-side mill with an internal whizzer classifier. (*ABB Raymond Div., Combustion Engineering Inc.*)

admitted inside the ball row and is fed through the grinding elements by centrifugal force. The Type E pulverizer is particularly suited to the direct firing of rotary kilns and industrial furnaces when close temperature control is required and long periods of continuous operation are essential. It is built in 17 sizes with capacities up to 12.6 Mg/h (14 tons/h) or more.

The Raymond ring-roller mill (Fig. 20-50) is of the internal air-classification type. The base of the mill carries the grinding ring, rigidly fixed in the base and lying in the horizontal plane. Underneath the grinding ring are tangential air ports through which the air enters the grinding chamber. A vertical shaft driven from below carries the roller journals. Centrifugal force urges the pivoted rollers against the ring. The raw material from the feeder drops between the rolls and ring and is crushed. Both centrifugal air motion and plows move the coarse feed to the nips. The air entrains fines and conveys them up from the grinding zone, providing some classification at this point. An air classifier is also mounted above the grinding zone to return oversize.

The method of classification used with Raymond mills depends on the fineness desired. If a medium-fine product is required (up to 85 or 90 percent through a No. 100 sieve), a single-cone air classifier is used. This consists of a housing surrounding the grinding elements with an outlet on top through which the finished product is discharged. This is known as the low-side mill. For a finer product and when frequent changes in fineness are required, the whizzer-type classifier is used. This type of mill is known as the *high-side mill.*

The Raymond ring-roll mill with internal air classification is used for the large-capacity fine grinding of most of the softer nonmetallic minerals. Materials with a Mohs-scale hardness up to and including 5 are handled economically on these units. Typical natural materials handled include barites, bauxite, clay, gypsum, magnesite, phosphate rock, iron oxide pigments, sulfur, talc, graphite, and a host of similar materials. Many of the manufactured pigments and a variety of chemicals are pulverized to high fineness on such units. Included are such materials as calcium phosphates, sodium phosphates, organic insecticides, powdered cornstarch, and many similar materials. When properly operated under suction, these mills are entirely dust-free and

automatic. They are available in nine basic sizes. Connected power ranges from 10 to 400 kW (15 to 600 hp). Capacities range from 0.5 to 450 Mg/h (0.5 to 50 tons/h), depending upon nature of material and exact fineness of grind.

The **Bradley pneumatic** (air-swept type) **Hercules mills** (*Bradley Pulverizer Co.*) are centrifugal ring-roll-type pulverizing mills which can be fitted with either two or three rolls. These mills are suitable for the pulverization of many materials to produce as coarse as 98 percent minus-20 mesh to as fine as 99.5 percent minus-325 mesh. The size of the pulverized product can be varied by adjusting the fineness selector mounted on top of the mill. Capacities range from 225 kg/h (500 lb/h) to 90 Mg/h (100 tons/h). When combined with the superfine *Bradley RMC classifier,* this mill can make a product finer than 11 μm.

The Williams ring-roller mill (*Williams Patent Crusher & Pulverizer Co.*) is an air-swept mill with integral classifier of the rotating-blade type (the Spinner air classifier) or a double-cone type. The fluid-bed roller mill system has jets to introduce hot air into the bed of coal in the mill to dry it.

Of similar design is the **Raymond VR mill,** which is designed to run with hot gases to simultaneously dry and grind. It accepts feed as large as 3 in.

The **MBF pulverizer** (*Foster Wheeler Corp.*) for coal grinding also has three grinding rollers pivoted off the grinding housing. These pulverizers are commonly used in the utility industry, and capacities of up to 80 Mg/h (90 tons/h) are available.

Bowl Mills In the Raymond bowl mill the journals that carry the grinding rollers are stationary while the grinding ring rotates. The grinding pressure is produced by means of springs, which may be adjusted to give the required pressure, and the distance between the rollers and the ring may be set to a predetermined clearance. The rollers do not touch the ring, there being no metal-to-metal contact.

DISK ATTRITION MILLS

The disk or attrition mill is a modern counterpart of the early buhrstone mill. Stones are replaced by steel disks mounting interchangeable metal or abrasive grinding plates rotating at higher speeds, thus permitting a much broader range of application. They have a place in the grinding of tough organic materials, such as wood pulp and corn grits. Grinding takes place between the plates, which may operate in a vertical or a horizontal plane. One or both disks may be rotated; if both, then in opposite directions. The assembly, comprising a shaft, disk, and grinding plate, is called a **runner.** Feed material enters a chute near the axis, passes between the grinding plates, and is discharged at the periphery of the disks. The grinding plates are bolted to the disks; the distance between them is adjustable.

The **Andritz-Sprout-Bauer attrition mill** (Fig. 20-51) is available in single- and double-runner models with 30- to 91-cm- (12- to 36-in.-) diameter disks and with power ranging up to 750 kW (1000 hp). By the use of a variety of plates and shell constructions these units are represented in such applications as coarse granulating, pulverizing, and shredding.

In general, single-runner mills are used for the same purposes as double-runner mills, excepting that they will accept a coarser feedstock, their range of reduction for a given material is more limited, and they offer correspondingly higher outputs at lower power. While spike-tooth plates can be used in certain applications to simulate hammer-mill action, they are more generally applied to specialized tasks involving tearing, shredding, or controlled shattering, as in dehulling, and in wet corn-milling, where the germ must be separated from the starchy part and the hulls. The performance data presented in Table 20-25 typify the applications of the attrition mill.

Buhrstone mills are attrition mills with hard circular stones serving as grinding media, generally French, American, Esopus buhrstones, or rock emery. Buhrstone mills are still employed for grinding special cereals and grains. Feed enters the mill through a center hole in one of the stones. It is distributed between the stone faces and ground while working its way to the periphery.

DISPERSION AND COLLOID MILLS

When the problem is to disrupt lightly bonded clusters or agglomerates, a new aspect of fine grinding enters. This may be illustrated by the breakdown of pigments to incorporate them in liquid vehicles in the making of paints, and the disruption of biological cells to release soluble products. Purees, food pastes, pulps, and the like are processed by this type of mill. Dispersion is also associated with the formation of emulsions which are basically two-fluid systems. Syrups, sauces, milk, ointments, creams, lotions, and asphalt and water-paint emulsions are in this category.

Mills employed for dispersion and colloidal operations operate on the principle of high-speed fluid shear. They produce dispersed droplets of fine size, around 3 to 5 μm.

Paint-grinding roller mills (Fig. 20-52) consist of two to five smooth rollers (sometimes called rolls) operating at differential speeds. A paste is fed between the first two, or low-speed, rollers and is discharged from the final, or high-speed, roller by a scraping blade. The paste passes from the surface of one roller to that of the next because of the differential speed, which also applies shear stress to the film of

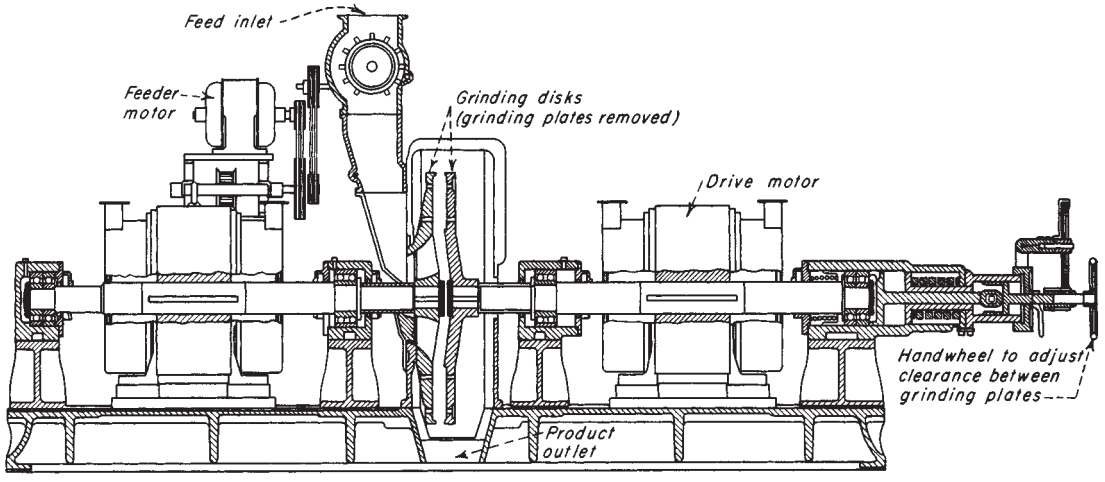


FIG. 20-51 Double-runner attrition mill. (*Andritz-Sprout-Baner Inc.*)

TABLE 20-25 Performance of Disk Attrition Mills

Material	Size-reduction details	Unit*	Capacity lb./hr.	Hp.
Alkali cellulose	Shredding for xanthation	B	4,860	5
Asbestos	Fluffing and shredding	C	1,500	50
Bagasse	Shredding	B	1,826	5
Bronze chips	⅛ in. to No. 100 sieve size	A	50	10
Carnauba wax	No. 4 sieve to 65% < No. 60 sieve	D	1,800	20
Cast-iron borings	¼ in. to No. 100 sieve	A	100	10
Cast-iron turnings	¼ in. to No. 100 sieve	E	500	50
Coconut shells	2 × 2 × ¼ in. to 5/100 sieve	B	1,560	17
	5/100 sieve to 43% < No. 200 sieve	D	337	20
Cork	2/20† sieve to 20/120 < No. 200 sieve	D	145	15
Corn cobs	1 in. to No. 10 sieve	F	1,500	150
Cotton seed oil and solvent	Oil release from 10/200 sieve product	B	2,400	30
Mica	4 × 4 × ¼ in. to 3/60 sieve	B	2,800	6
	8/60 to 75% < 60/200 sieve	D	510	7.5
Oil-seed cakes (hydraulic)	1½ in. to No. 16 sieve	F	15,000	100
Oil-seed residue (screw press)	1 in. to No. 16 sieve size	F	25,000	100
Oil-seed residue (solvent)	¼ in. to No. 16 sieve	F	35,000	100
Rags	Shredding for paper stock	B	1,440	11
Ramie	Shredding	B	820	10
Sodium sulfate	35/200 sieve to 80/325 sieve	B	11,880	10
Sulfite pulp sheet	Fluffing for acetylation, etc.	C	1,500	50
Wood flour	10/50 sieve to 35% < 100 sieve	D	130	15
Wood rosin	4 in. max. to 45% < 100 sieve	B	7,200	15

*A—8 in. single-runner mill D—20 in. double-runner mill
B—24 in. single-runner mill E—24 in. double-runner mill
C—36 in. single-runner mill F—36 in. double-runner mill
†2/20, or smaller than No. 2 and larger than No. 20 sieve size.
NOTE: To convert inches to centimeters, multiply by 2.54; to convert pounds per hour to kilograms per hour, multiply by 0.4535; and to convert horsepower to kilowatts, multiply by 0.746.

material passing between the rollers. Roller-mill technique and action have been studied by Hummel [*J. Oil Colour Chem. Assoc.*, 270–277 (June 1950)], and the breakup of agglomerates in this mill has been discussed by Krekel [*Chem. Ing. Tech.*, **38**(3), 229 (1966)].

Colloid mills which are employed for dispersion or for emulsification fall into four main groups: the hammer or turbine, the smooth-surface disk, the rough-surface type, and valve or orifice devices.

A mathematical analysis of the action in **Kady** and other colloid mills checks well with experimental performance [Turner and McCarthy, *Am. Inst. Chem. Eng. J.*, **12**(4), 784 (1966)]. Various models of the Kady mill have been described, and capacities and costs given by Zimmerman and Lavine [*Cost Eng.*, **12**(1), 4–8 (1967)]. Energy requirements differ so much with the materials involved that other devices are often used to obtain the same end. These include high-speed stirrers, turbine mixers, bead mills, and vibratory mills. In some cases, sonic devices are effective.

The concentration of energy in mills of this class is high, and there is a considerable amount of heating. This is materially reduced by use of a cooling-water jacket. In other cases, as when emulsions are made hot, the jacket is employed for heating.

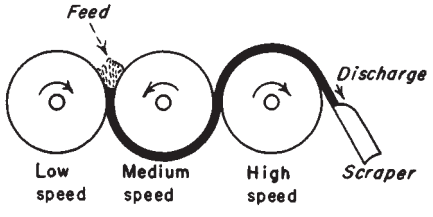


FIG. 20-52 Roller mill for paint grinding.

The **Morehouse mill** (*Morehouse Industries, Inc.*) is a high-speed disk type of mill (Fig. 20-53). The undispersed phase is fed at the top and passes between converging disks, being thrown outward at the periphery.

In the **Premier Mill** the rotor is shaped like the frustrum of a cone, similar to that in Fig. 20-53. Surfaces are smooth, and adjustment of the clearance can be made from 25 μm (0.001 in) upward. A small impeller helps to feed material into the rotor gap. The mill is jacketed for temperature control. Direct-connected liquid-type mills are available with 15- to 38-cm (6- to 15-in) rotors. These mills operate at 3600 r/min at capacities up to 2 m^3/h (500 gal/h). They are powered with up to 28 kW (40 hp). Working parts are made of Invar alloy, which does not expand enough to change the grinding gap if heating occurs. The rotor is faced with Stellite or silicon carbide for wear resistance. For pilot-plant operations, the Premier Mill is available with 7.5- and 10-cm (3- and 4-in) rotors. These mills are belt-driven and operate at 7200 to 17,000 r/min with capacities of 0.02 to 2 m^3/h (5 to 50 gal/h).

The **Charlotte mill** (*Chemicolloid Corp.*) also employs high speed of rotation with the fluid flowing between a grooved conical rotor and a corresponding grooved conical stator. Clearance between them is regulated by an external calibrated adjustment device. Laboratory model W-10 operates at 0.75 kW (1 hp) with a capacity of 4 to 190 L/h (1 to 50 gal/h). Sanitary models are available for processing foodstuffs.

The **APV Gaulin colloid mill** has a smooth rotor, shaped like a discus.

A **high-pressure valve homogenizer** such as the Gaulin and Rannie (APV Gaulin Group) forces the suspension through a narrow orifice. The equipment has two parts: a high-pressure piston pump and a homogenizer valve [Kula and Schuette, *Biotechnology Progress*, **3**(1), 31–42 (1987)]. The pump in production machines may have up to 6 pistons. The valve, illustrated in Fig. 20-54, opens at a preset or adjustable value, and the suspension is released at high velocity (300 m/sec) and impinges on an impact ring. The flow changes direction twice by 90 degrees, resulting in turbulence. Machines studied so far compress up to 60 Mpa, but higher pressures are becoming available. For machines with feed rates greater than 2000 L/h and pressures up to 100 Mpa tungsten carbide or special ceramics are used for the valve components to reduce erosion. There is also a 2-stage valve, but it has been shown better to expend all the pressure across a single stage.

The temperature of the suspension increases about 2.5°C per 10 Mpa pressure drop. Therefore intermediate cooling is required for

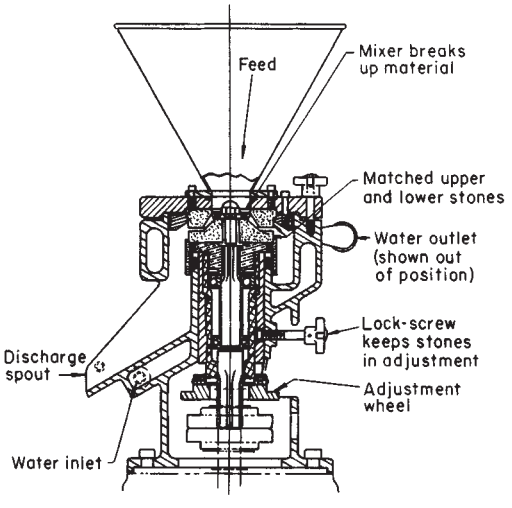


FIG. 20-53 Model M colloid mill. (*Morehouse Industries, Inc.*)

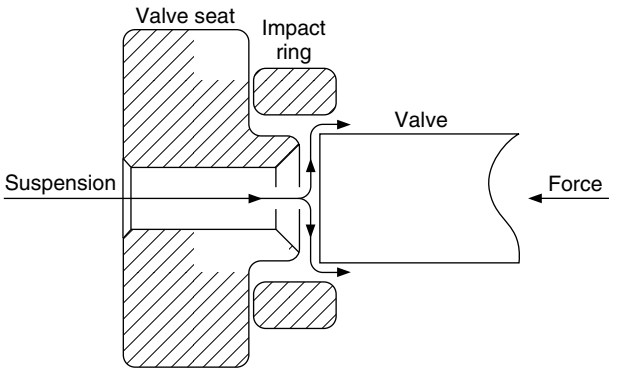


FIG. 20-54 Details of valve seat of the Gaulin high-pressure homogenizer, type CD.

multiple passes. In the Gaulin M3 homogenizer operated with a feed rate of 400 L/h and a pressure of 55 Mpa around 6000 kcal/hr have to be removed by a cooling system.

These units have been used to disrupt bacterial cells for release of enzymes. (See "Cell Disruption.")

FLUID-ENERGY OR JET MILLS

A detailed description of mills of this type has been presented by Gossett [*Chem. Process.* (Chicago), **29**(7), 29 (1966)]. **Fluid-energy mills** may be classified in terms of the nature of the mill action. In one class of mills, the fluid energy is admitted in fine high-velocity streams at an angle around a portion or all of the periphery of a grinding and classifying chamber. In this class are the Micronizer, jet pulverizer, Reductionizer, Jet-O-Mizer, and others of somewhat similar structure. In the other class the fluid streams convey the particles at high velocity into a chamber where two streams impact upon each other. The **Majac** and the **Fluidized-Bed Jet** mills are in this class. Whether the particles are conveyed with the jet or are intercepted by jets, there is a high-energy release and a high order of turbulence which causes the particles to grind upon themselves and to be ruptured. Not all the particles are fully ground; so it is necessary to carry out a classifying operation and to return the oversize for further grinding. Most of these mills utilize the energy of the flowing-fluid stream to effect a centrifugal classification. The Majac mill differs, using a mechanical air classifier.

The **Micronizer** (*Sturtevant Inc.*) consists of a shallow circular grinding chamber in which the material to be pulverized is acted upon by a number of gaseous fluid jets issuing through orifices spaced around the periphery of the chamber. The rotating gas must discharge at the center, carrying the fines with it, while the coarse particles are thrown toward the wall, where they are subjected to further reduction by impact from particles entrained by incoming jets.

The action in these mills has been studied photographically and mathematically [Rumpf, *Chem. Ing. Tech.*, **32**(3), 129–135; (5), 335–342 (1960); *ATS translations*, 668GJ, 844GJ].

Micronizer mills are constructed in nine standard sizes from 5 to 107 cm (2 to 42 in) in diameter, with capacities from 250 g/h to 1.8 Mg/h (½ lb/h to 2 tons/h). The feed size should be smaller than 1 cm (¼ in). Production rate, fluid consumption, and fineness figures are shown in Table 20-26.

The **jet pulverizer** (*Jet Pulverizer Co.*) is another mill of the shallow-pan, angle-jet, and radial-inward-classification type, like the Micronizer.

The **Jet-O-Mizer** (*Fluid Energy Processing & Equipment Co.*) is one of a group employing a hollow elongated torus which is placed vertically. The operating principle is similar to that of the Micronizer, with the feed entering tangentially to the whirling fluid stream and the fines leaving centrally.

TABLE 20-26 Micronizer Performance*

Material	Product average size, μm	Feed		Fluid consumption, g fluid/g solid	
		Size sieve no.	Rate, lb/h	Air	Steam
Ceylon graphite	2	3	200	—	8.5
Cryolite	3	60	900	—	4.0
Limestone	3.5	80	1000	—	4.0
Hard talc	3.5	20	1000	—	4.0
Silica gel	5.5	8	500	—	3.5
Soft talc	6.5	20	1800	—	2.5
Barite	3.5	40	1800	—	2.2
Bituminous coal	2	10	1300	—	1.2
Copal resin	5	2	600	7.5	
Wolframite ore	5.5	10	800	5.6	
Sulfur	3.5	3	1300	3.5	

Ind. Eng. Chem.*, **38, 672 (1946). To convert pounds per hour to kilograms per hour, multiply by 0.4535.

Trost air mills from *Colt Industries* are available in five sizes. The smallest mill (Gem T) is a research unit and can be used for fine-grinding studies. Capacities of 1 to 2300 kg/h (2 to 5000 lb/h) are available. Air-flow rates vary from 0.2 to 28 m^3/min (6.5 to 1000 ft^3/min).

The **Majac jet pulverizer** (*Hosokawa Micron Powder Systems Div.*) is an opposed-jet type with a mechanical classifier (Fig. 20-55). Fineness is controlled primarily by the classifier speed and the amount of fan air delivered to the classifier, but other effects can be achieved by variation of nozzle pressure, distance between the muzzles of the gun barrels, and position of the classifier disk. These pulverizers are available in 30 sizes, operated on quantities of compressed air ranging from approximately 0.6 to 13.0 m^3/min (20 to 4500 ft^3/min). In most applications, the economics of the use of this type of jet pulverizer becomes attractive in the range of 98 percent through 200 mesh or finer.

Materials illustrated in Table 20-27 are shown because of their wide range and type.

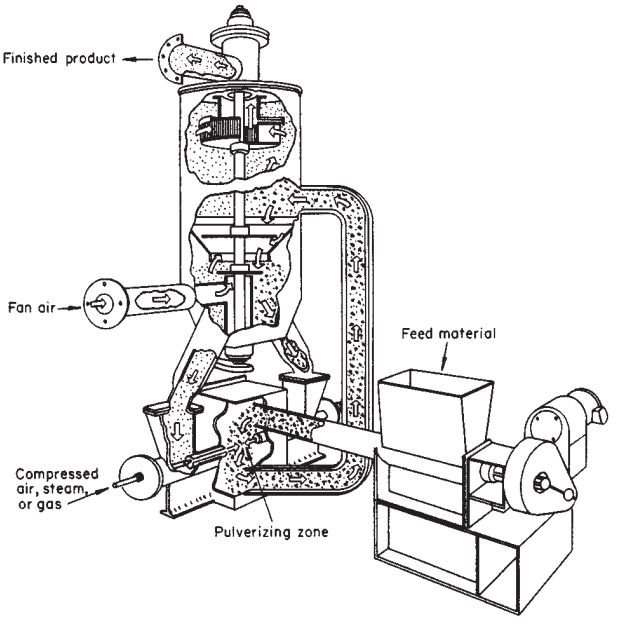


FIG. 20-55 Majac jet pulverizer. (*Hosokawa Micron Powder Systems Div.*)

TABLE 20-27 Majac Jet Pulverizer Capacities*

Material	Finished particle size	Mill size	Production, lb h	Grinding fluid used
Alumina	–325 mesh, 3 μm average	15	12,000	6300 lb/h steam at 100 psig, 750°F.
Coal, bituminous	90%, –325 mesh	20	8,000	3000 ft³/min air at 100 psig, 70°F.
Diphenyl phthalate	–325 mesh, 20–30 μm maximum, 4.2 μm average	2–6	435	300 ft³/min air at 100 psig, 70°F.
Feldspar, silica	99%, –200 mesh	15	8,500	1350 ft³/min air at 100 psig, 800°F.
Graphite	90%, –10 μm	8.5–2.5	50	75 ft³/min air at 100 psig, 70°F.
Mica	95%, –325 mesh	8	1,600	720 ft³/min air at 100 psig, 800°F.
Rare-earth ore	60%, –1 μm	8–15	400	720 ft³/min air at 100 psig, 800°F.

*°C = (°F – 32) × 5/9. To convert pounds per hour to kilograms per hour, multiply by 0.4535; to convert pounds per square inch gauge to kilopascals, multiply by 7.0.

Fluidized-bed opposed-jet mills (*Hosokawa Micron Powder Systems Div.*) differ from the Majac mill in that powder is not fed into the jets, but the jets impinge into a chamber which contains suspended powder. The powder is entrained into the jets. This eliminates wear on the nozzles, and reduces contamination. Otherwise, construction and applications are similar to the Majac mill. The fluidized-bed level is maintained a few inches above the jets. The Fluidized-bed mill is available in 13 sizes with air volumes ranging from 50 to 11,000 m³/h. One application is for toner grinding.

NOVEL METHODS

Only once in 15 years does a truly novel method of size reduction become successful. The roll press is a truly successful example of a novel mill, and stirred-bead mills are older mills that have reached a new state of development. Many more methods are proposed and studied; some of these are described below. The information may be useful to judge other novel methods that may be proposed.

Avoiding Size Reduction Since size reduction is a difficult and inefficient operation, it is sometimes better to avoid it and use another approach. Thus rather than make large crystals and then grind them, one may be able to precipitate or crystallize material in the desired fine size. It may even be possible to control the process to give a more narrow size distribution than would be possible by size reduction.

In the case of lactose manufacture, crystals of uniform size are produced by first grinding part of a previous batch and taking a quantity with the required number of particles, then introducing these as seed crystals into a solution that is gradually cooled with gentle stirring. Variation in size of the seed crystals does not affect the size of the product crystals.

Some materials that are prepared in the molten state are converted advantageously to flake form by cooling a thin layer continuously on the surface of a rotating drum. Another way is to spray cool from the melt, using a spray dryer with cold air. Thus, massive cooling and subsequent pulverizing are avoided. See the Index for details of these other methods.

Ultrafine powders can be prepared in high-temperature plasmas. Particles below 1 μm and larger particles with unusual surface structures are formed according to Waldie [*Trans. Inst. Chem. Eng.*, **48**(3), T90 (1970)]. Energy costs are discussed.

Bond [*Min. Eng.* (*London*), **60**(1), 63–64 (1968)] reviewed attempts to induce breakage without wastefully applying pressure and concluded that inherent practical limitations have been found for the following methods: spinning particles, resonant vibration, electrohydraulic crushing, induction heating, sudden release of gas pressure, and chisel-effect breakers. For a review of more recent efforts, see edition 6 of this handbook.

CRUSHING AND GRINDING PRACTICE

CEREALS AND OTHER VEGETABLE PRODUCTS

Flour and Feed Meal The **roller mill** is the traditional machine for grinding wheat and rye into high-grade flour. A typical mill used for this purpose is fitted with two pairs of rolls, capable of making two separate reductions. After each reduction the product is taken to a bolting machine or classifier to separate the fine flour, the coarse product being returned for further reduction. Feed is supplied at the top, where a vibratory shaker spreads it out in a thin stream across the full width of the rolls.

Rolls are made with various types of corrugation. Two standard types are most generally used: the dull and the sharp, the former mainly on wheat and rye, and the latter for corn and feed. Under ordinary conditions, a sharp roll is used against a sharp roll for very tough wheat, a sharp fast roll against a dull slow roll for moderately tough wheat, a dull fast roll against a sharp slow roll for slightly brittle wheat, and a dull roll against a dull roll for very brittle wheat. The speed ratio usually is 2½:1 for corrugated rolls and 1¼:1 for smooth rolls. By examining the marks made on the grain fragments it has been concluded (Scott, *Flour Milling Processes*, Chapman & Hall, London, 1951) that the differential action of the rolls actually can open up the berry and strip the endosperm from the hulls.

High-speed **hammer** or **pin mills** result in some *selective grinding*. Such mills combined with air classification can produce fractions with controlled protein content. An example of such a combination is a Bauer hurricane hammer mill combined with the Alpine Mikroplex superfine classifier. Flour with different protein content is needed for the baking of breads and cakes, and these types of flour were formerly available only by selection of the type of wheat, which is limited by growing conditions prevailing in particular locations [Wichser, *Milling*, **3**(5), 123–125 (1958)].

Soybeans, Soybean Cake, and Other Pressed Cakes After granulation on rolls the granules are generally treated in presses or solvent extracted to remove the oil. The product from the presses goes to attrition mills or flour rolls and then to bolters, depending upon whether the finished product is to be a feed meal or a flour.

The method used for grinding pressed cakes depends upon the nature of the cake, its purity, residual oil, and moisture content. If the whole cake is to be pulverized without removal of fibrous particles, it may be ground in a hammer mill with or without air classification. A 15-kW (20-hp) hammer mill with an air classifier, grinding pressed cake, had a capacity of 136 kg/h (300 lb/h), 90 percent through No. 200 sieve; a 15-kW (20-hp) screen-hammer mill grinding to 0.16-cm (1/16-in) screen produced 453 kg/h (1000 lb/h). In many cases the hammer mill is used merely as a preliminary disintegrator, followed by an attrition mill. Typical performance of the attrition mill is given in Table 20-25. A finer product may be obtained in a hammer mill in closed circuit with an external screen or classifier.

High-speed hammer mills are extensively used for the grinding of soya flour. For example, the Raymond Imp mill with an air classifier is used, primarily with solvent-extracted soya.

Starch and Other Flours Grinding of starch is not particularly difficult, but precautions must be taken against explosions; starches must not come in contact with hot surfaces, sparks, or flame when sus-

pended in air. See "Properties of Solids: Safety" for safety precautions. When a product of medium fineness is required, a hammer mill of the screen type is employed. Potato flour, tapioca, banana, and similar flours are handled in this manner. For finer products a high-speed impact mill such as the Entoleter pin mill is used in closed circuit with bolting cloth, an internal air classifier, or vibrating screens.

ORES AND MINERALS

Metalliferous Ores The most extensive grinding operations are done in the ore-processing and cement industries. Grinding is one of the major problems in milling practice and one of the main items of expense. Mill manufacturers, operators, and engineers find it necessary to compare grinding practice in one plant with that of another, attempting to evaluate circuits and practices (Arbiter, *Milling in the Americas,* 7th International Mineral Processing Congress, Gordon and Breach, New York, 1964). Direct-shipping ores are high in metal assay, and require only preliminary crushing before being fed to a blast furnace or smelter. As these high-grade ores have been depleted, it has become necessary to concentrate ores of lower mineral value. The native copper ores of Michigan have given way to porphyry copper ores of the southwest. Initially the deposits containing 2 to 4 percent copper were worked, but now ores of 0.40 percent must be processed by grinding and flotation or leaching. The effectiveness of closed-circuit milling with wet classifiers reopened the Iron Range of Minnesota by permitting economic beneficiation of taconite iron ores, which contain up to two-thirds hard cherty gangue. By grinding, magnetic separation or froth flotation and pelletizing, a blast-furnace feed is produced that is more uniform and gives a higher iron yield than the direct-shipping ores.

Three types of milling circuits are used in large ore-processing plants [Allis Chalmers, *Engineering & Mining J.,* **181**(6), 69–171 (1980)]. (1) Three stages of gyratory crushers, followed by a wet rod mill followed by a ball mill (Fig. 20-56). This combination has high-power efficiency and low steel consumption, but higher-investment cost because rod mills are limited in length to 20 ft by potential tangling of the rods. (2) Similar crusher equipment followed by one or two stages of large ball mills. One stage may suffice if product size can be as coarse as 65 mesh. This circuit has lower capital cost but higher energy and wear costs. (3) One stage of gyratory crusher followed by large-diameter semiautogenous ball mills followed by a second stage of autogenous or ball mills (Fig. 20-57). The advantage of autogenous mills is reduction of ball-wear costs, but power costs are at least 25 percent greater, because

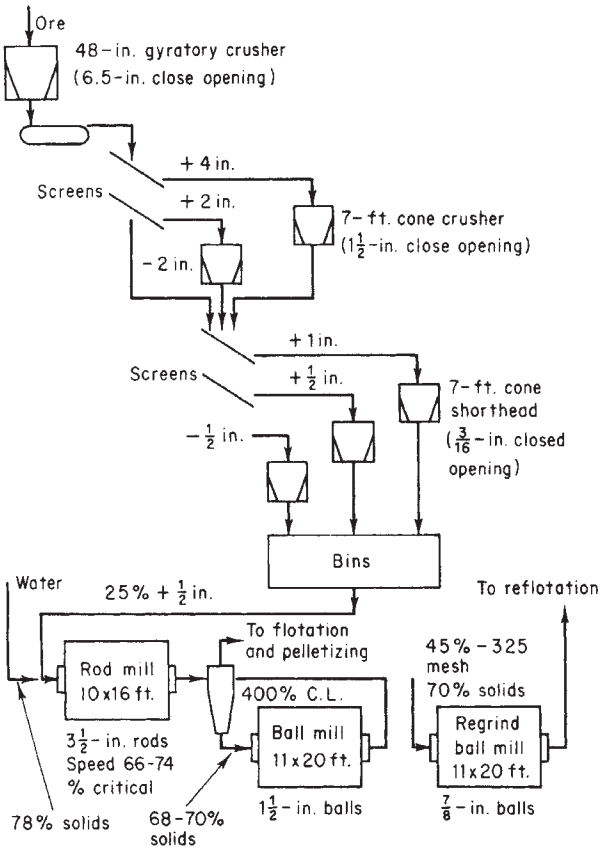


FIG. 20-56 Ball- and rod-mill circuit. Simplified flow sheet of the Cleveland-Cliffs Iron Co. Republic mine iron-ore concentrator. To convert inches to centimeters, multiply by 2.54; to convert feet to centimeters, multiply by 30.5. (*Johnson and Bjorne,* Milling in the Americas, *Gordon and Breach, New York, 1964.*)

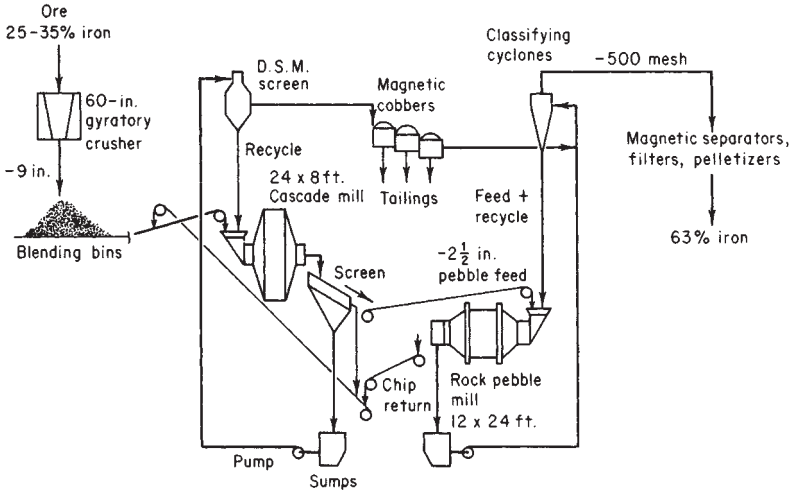


FIG. 20-57 Autogenous mill circuit. Simplified flow diagram of the Cleveland-Cliffs Iron Co. Empire iron-mine concentrator with two autogenous wet-grinding stages. To convert inches to centimeters, multiply by 2.54; to convert feet to centimeters, multiply by 30.5.

irregular-shaped media are less effective than balls. A fourth circuit using the roll press has been widely accepted in the cement industry (see "Roll Press" and "Cement Industry"), and could be used in other mineral plants. It could replace the last stage of crushers and the first stage of ball or rod mills, at substantially reduced power and wear.

A flow sheet for one iron ore process is shown in Fig. 20-56. For the grinding of softer copper ore the rod mill might be eliminated, both coarse-crushing and ball-milling ranges being extended to fill the gap.

Autogenous milling of iron and copper ores has been widely accepted. When successful, this method results in economies due to elimination of media wear. Probably another reason for efficiency is the use of higher circulating loads and better classification. These improvements resulted from the need to use larger-diameter mills to obtain grinding with rock media that have a lower density than steel balls. The major difficulty is in arranging the crushing circuits and the actual mining so as to assure a steady supply of large ore lumps to serve as grinding media. With rocks that are too friable this cannot be achieved.

With other ores there has been a problem of buildup of intermediate-sized particles, but this has been solved either by adding a small load of steel balls, thus converting to a semiautogenous grinding system (SAG), or by sending the scalped intermediate-sized particles through a cone crusher. A flow sheet for a typical wet autogenous circuit is shown in Fig. 20-57.

Nonmetallic Minerals Dry and wet grinding processes are used. **Dry grinding** is less expensive than wet grinding in the coarser sizes because a dry product is obtained without a final drying step. Dry grinding is carried out with ball, pebble, roller, and hammer mills with closed-circuit air classification. The product may be 99.8 percent through a 325-mesh sieve. Jet mills can produce a product in the range 5 to 15 μm, but at greater cost.

Wet processes use continuous ball and pebble mills, stirred and vibratory media mills, and pug mills. Wet processes take advantage of more effective classification in water, using bowl and cone classifiers, hydroseparators, thickeners, continuous centrifuges and cyclones, vacuum filters, and rotary, tray, or tunnel dryers. After drying, the cake generally has to be broken up in some type of disintegrator or pulverizer unless it was spray-dried. The objective of a process may be to obtain many grades of the same material by tying classifiers and screens into the grinding system to remove various-sized products. Choice of equipment generally depends on (1) hardness and (2) contaminations. Capacity of any system decreases rapidly with increasing fineness of the material; this applies particularly to nonmetallics, for which extreme fineness is usually required.

Clays and Kaolins Because of declining quality of available clay deposits, beneficiation is becoming more required [Uhlig, *Ceramics Forum International*, **67**(7–8), 299–304 (1990), English and German text]. Beneficiation normally begins with a size-reduction step, not to break particles but to dislodge adhering clay from coarser impurities. In **dry processes** this is done with low-energy impact mills.

Mined clay with 22 percent moisture is broken up into pieces of less than 5 cm (2 in) in a rotary impact mill without screen, and fed to a rotary gas-fired kiln for drying (see Fig. 20-58). The moisture content is then 8 to 10 percent, and this material is fed to a mill, usually a Raymond ring-roll mill with an internal whizzer classifier or a pan mill. Hot gases introduced to the mill complete the drying while the material is being pulverized to the required fineness.

To grind 3.2 Mg/h (3½ tons/h) of a raw clay, power consumption will be about 75 kW (100 hp), and it takes about 31 m^3 (1100 ft^3) of natural gas 3.7 MJ/m^3 (1000 Btu/ft^3) to dry the clay from 10 percent moisture down to about 1 percent. The product is used in paint pigments and rubber fillers.

Larger amounts of clay are being produced in dry powdered form [Anon., *Ceramics Forum International*, **67**(7–8), 330–4 (1990)]. After grinding, the clay is agglomerated to a flowable powder with water mist in a balling drum.

In the **wet process,** the clay is masticated in a pug mill to break up lumps and then dispersed with a dispersing aid and water to make a 40 percent solids slip of low viscosity. A high-speed agitator such as a Cowles dissolver is used for this purpose. Sands are settled out, and then the clay is classified into two size fractions in either a Hydrosettler or a continuous Sharples or Bird centrifuge. The fine fraction, with sizes of less than 1 μm, is used as a pigment and for paper coating, while the coarser fraction is used as a paper filler.

A process for upgrading kaolin by grinding in a stirred bead mill has been reported (Stanczyk and Feld, *U.S. Bur. Mines Rep. Invest.* 6327 and 6694, 1965). By this means the clay particles are delaminated, and the resulting platelets give a much improved surface on coated paper.

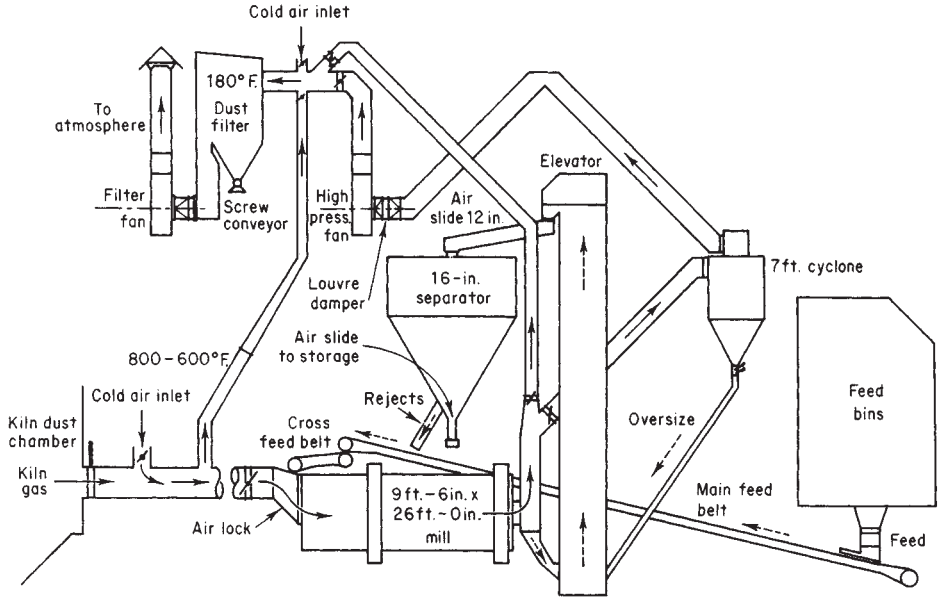


FIG. 20-58 Combined drying-grinding system using ball-mill and hot kiln exhaust gases. To convert inches to centimeters, multiply by 2.54; to convert feet to centimeters, multiply by 30.5; °C = (°F − 32) × 5/9. [*Tonry,* Pit Quarry (*February-March 1959*).]

Talc and Soapstone Generally these are easily pulverized. Certain fibrous and foliated talcs may offer greater resistance to reduction to impalpable powder, but these are no longer produced because of their asbestos content.

Talc milling is largely a grinding operation accompanied by air separation. Most of the industrial talcs are dry-ground. Dryers are commonly employed to predry ahead of the milling operation because the wet material reduces mill capacity by as much as 30 percent.

Conventionally, in talc milling, rock taken from the mines is crushed in primary and then in secondary crushers to at least 1.25 cm (½ in) and frequently as fine as 0.16 cm (1/16 in).

Ring-roll mills with internal air separation are widely used for the large-capacity fine grinding of the softer talcs. High-speed hammer mills with internal air separation are also an outstanding success on some of the softer high-purity talcs for very fine fineness.

The mills in the western United States, in which generally are ground softer talcs than those of New York, have simple flow sheets. Single-stage crushing is employed, and the talc is merely ground in Raymond roller mills in closed circuit with air separators.

For a ring-roller mill receiving 2.54-cm (1-in) feed, production rates range from 1360 to 2720 kg/h (3000 to 6000 lb/h) for 60-kW (80-hp) grinding to 99 to 99.5 percent able to pass a No. 200 sieve.

Talcs of extreme fineness and high surface area are rapidly attaining industrial importance and are used for various purposes in the paint, paper, plastics, and rubber industries.

Carbonates and Sulfates Carbonates include limestone, calcite, marble, marls, chalk, dolomite, and magnesite; the most important sulfates are barite, celestite, anhydrite, and gypsum; these are used as fillers in paint, paper, and rubber. (Gypsum and anhydrite are discussed below as part of the cement, lime, and gypsum industries.)

A Raymond 5057 ring-roller mill pulverizing fluorspar produces 4500 kg (10,000 lb) of product per hour 95 percent minus 200 mesh with 104 kW (140-hp) operating power, or 26 kWh/Mg (23.4 kWh/ton). Fluorspar is also ground in continuous-tube mills with classification.

Silica and Feldspar These are ground in silex-lined mills with flint balls (see Table 20-28). At a mine near Cairo, Illinois, silica is successfully crushed prior to ball-milling in American rotary impact mills having loose crushing rings made of hard alloy steel. The rings are easily replaced as they wear.

Feldspar for the ceramic and chemical industries is ground finer than for the glass industry. A feldspar mill is described in U.S. Bur. Mines Cir. 6488, 1931. It uses pebble mills with a Gayco air classifier.

Table 20-28 gives the results obtained with Hardinge pebble mills, grinding several siliceous refractory materials.

Asbestos and Mica Asbestos is no longer mined in the United States because of the severe health hazard, but it is still mined and processed in Canada. See previous editions of this handbook for process descriptions.

The micas, as a class, are difficult to grind to a fine powder; one exception is disintegrated schist, in which the mica occurs in minute flakes. For dry grinding, hammer mills equipped with an air-transport system are generally used. Maintenance is often high. It has been established that the method of milling has a definite effect on the particle characteristics of the final product. Dry grinding of mica is customary for the coarser sizes down to 100 mesh. Micronized mica, produced by high-pressure steam jets, is considered to consist of highly delaminated particles.

Conditions for grinding micas and kaolin in a Drais stirred-bead mill were investigated [Sivamohan and Vachot, *Powder Technology,* **61**(2), 119–129 (1990)]. Muscovite with a high aspect ratio of 50:1 imparts strength and electrical breakdown resistance to molded-plastic parts. A feed material with d_{90} of 180 μm and aspect ratio 3:1 was ground in 1 to 10 passes with 4 min residence time. It gave aspect ratio as high as 27:1 and d_{50} of 8 μm with the longest grinding times. Glass beads of 0.3 and 0.8 mm diameter had the same effect. Pulp density of 12 wt % gave better grinding rate than 25 percent. Low-dispersant concentration of 0.35 wt % was best.

Wollastonite with an aspect ratio of 15:1 is useful as a replacement for asbestos and as a high-strength filler for plastics. The feed material with d_{90} of 45 μm was similarly ground. Beads of 0.3 mm gave faster grinding than 0.8 mm beads, and these corresponded to a bead-particle-size ratio of 19, confirming other results.

Refractories Refractory bricks are made from fireclay, alumina, magnesite, chrome, forsterite, and silica ores. These materials are crushed and ground, wetted, pressed into shape, and fired. To obtain the maximum brick density, furnishes of several sizes are prepared and mixed. Thus a magnesia brick may be made from 40 percent coarse, 40 percent middling, and 20 percent fines. Theorems have been proposed for calculating weight ratios of sizes to produce maximum packing density of powder mixtures [Lewis and Goldman, *J. Am. Ceram. Soc.,* **49**(6), 323 (1966)]. Preliminary crushing is done in jaw or gyratories, intermediate crushing in pan mills or ring rolls, and fine grinding in open-circuit ball mills. Since refractory plants must make a variety of products in the same equipment, pan mills and ring rolls are preferred over ball mills because the former are more easily cleaned.

Sixty percent of refractory magnesite is made synthetically from Michigan brines. When calcined, this material is one of the hardest refractories to grind. Gyratory crushers, jaw crushers, pan mills, and ball mills are used.

Alumina produced by the Bayer process is precipitated and then calcined [Krawczyk, *Ceramic Forum International,* **67**(7–8), 342–8 (1990)]. Aggregates are typically 20 to 70 μm, and have to be reduced. The standard product is typically made in continuous dry ball or vibratory mills to give a product d_{50} size of 3–7 μm, 98 percent finer than 45 μm. The mills are lined with wear-resistant alumina blocks, and balls or cylinders are used with an alumina content of 80–92 percent. The products containing up to 96 percent Al_2O_3 are used for bricks, kiln furniture, grinding balls and liners, high voltage insulators, catalyst carriers, etc.

Ultrafine grinding is carried out batchwise in vibratory or ball mills, either dry or wet. The purpose of batch operation is to avoid the residence time distribution which would pass less-ground material through a continuous mill. The energy input is 20–30 times greater than for standard grinding, with inputs of 1300–1600 kWh/ton compared to 40–60. Jet milling is also used, followed by air classification, which can reduce top size below 8 μm.

TABLE 20-28 Grinding Refractory Siliceous Materials in Pebble Mills

	Feldspar	Silica sand	Enamel frit	Grog
Size of mill	8′ × 60″	8′ × 48″	4½′ × 16″	5′ × 22″
Feed size	2″	20 mesh	⅛″	1½″
Size of product	99% through No. 200 sieve	98% through No. 325 sieve	97% through No. 100 sieve	95% through No. 10 sieve
Capacity, tons/hr	1.75	1.25	0.225	5
Power for mill, hp	68	58	8.5	28
Power for auxiliaries, hp	21	20		
Pebble load, lb	10,000	12,000	2000	2800
Speed of mill, r.p.m.	22	18	30	30
Moisture, %	1	1	0	1
Type of classifier	Hardinge	Air	Trommel screen on mill	
Lining and grinding mediums		Flint blocks and flint pebbles	Steel	

NOTE: To convert feet to centimeters, multiply by 30.5; to convert inches to centimeters, multiply by 2.54; to convert tons per hour to megagrams per hour, multiply by 0.907; and to convert horsepower to kilowatts, multiply by 0.746.

Among new mill developments, annular-gap bead mills and stirred bead mills are being used. These have a high cost, but result in a steep particle-size distribution when used in multipass mode [Kolb, *Ceramic Forum International,* **70**(5), 212–216 (1993)]. Costs for fine grinding typically exceed the cost of raw materials. Products are used for high-performance ceramics.

Silicon carbide grains were reduced from 100–200 mesh to 80 percent below 1 μm in a version of stirred bead mill, using 20–30 mesh silicon carbide as media (Hoyer, Report Investigations U.S. Bureau Mines 9097, 9 pp., 1987).

Crushed Stone and Aggregate In-pit crushing is increasingly being used to reduce the rock to a size that can be handled by a conveyor system. In quarries with a long, steep haul, conveyors may be more economic than trucks. The primary crusher is located near the quarry face, where it can be supplied by shovels, front-end loaders or trucks. The crusher may be fully mobile or semimobile. It can be of any type listed below. The choices depend on individual quarry economics, and are described by Faulkner [*Quarry Management and Products,* **7**(6), 159–168 (1980)].

Primary crushers used are jaw, gyratory, impact, and toothed roll crushers. Impact mills are limited to limestone and softer stone. With rocks containing more than 5 percent quartz, maintenance of hammers may become prohibitive. Gyratory and cone crushers dominate the field for secondary crushing of hard and tough stone. Rod mills have been employed to manufacture stone sand when natural sands are not available.

Crushed stone for road building must be relatively strong and inert, and must meet specifications regarding size distribution and shape. Both size and shape are determined by the crushing operation. Table 20-29 lists specifications for a few size ranges.

The purpose of these specifications is to produce a mixture where the fines fill the voids in the coarser fractions, thus to increase load-bearing capacity. (See "Refractories" above.)

Sometimes a product that does not meet these requirements must be adjusted by adding a specially crushed fraction. No crushing device available will give any arbitrary size distribution, and so crushing with a small reduction ratio and recycle of oversize is practiced when necessary.

The claim of various crushers to produce a cubical product is exaggerated. However, there are differences. If an impact mill is designed to apply an excess of energy at each blow, then production of slivers can be avoided but a larger amount of fines is produced.

A survey of research on product shape and size distribution (**grading**) was given by Rösslein [translation by Shergold, *Quarry Managers J.,* 207–222 (October 1946)]. The main study involved tests on 30 jaw crushers, with shapes of over 1 million particles being measured. Concerning **particle shape,** there is a tendency for hard rocks to produce more numerous flaky chippings than soft rocks. The size of feed to a crusher does not affect the shape of products. With jaw crushers, the largest and finest sizes contain the highest proportion of flaky pieces, but even the intermediate sizes are irregular. An increase in the reduction ratio of jaw crushers increases the flakiness of the product. Smooth jaws produce more numerous flaky pieces than corrugated jaws. Curved jaws produce less fines but more numerous flaky particles. Crusher speed has little effect. The presence of material too small to be crushed has a deleterious effect on the shape of products. Secondary crushers with a small reduction ratio can improve the shape of primary crushed material, but secondary crushers are not inherently different from primary crushers. Slotted screens can remove flaky particles from the product. Impact crushers produce fewer flaky particles than any other type.

Grading of the product (i.e., size distribution) depends on the discharge opening, which is difficult to measure and adjust owing to wear of the plates in a jaw crusher. Size of feed and wear of plates do not affect grading significantly. Table 20-10 relates sizes of product to crusher settings.

FERTILIZERS AND PHOSPHATES

Many of the materials used in the fertilizer industry are pulverized, such as those serving as sources for calcium, phosphorus, potassium, and nitrogen. The most commonly used for their lime content are limestone, oyster shells, marls, lime, and, to a small extent, gypsum. Limestone is generally ground in hammer mills, ring-roller mills, and ball mills. Fineness required varies greatly from No. 10 sieve to 75 percent through No. 100 sieve.

Oyster Shells and Lime Rock Operating characteristics for hammer mills grinding oyster shells and burned lime for agricultural purposes are given in Table 20-30.

Phosphates Phosphate rock is generally ground for one of two major purposes: for direct application to the soil or for acidulation with mineral acids in the manufacture of fertilizers. Because of larger capacities and fewer operating-personnel requirements, plant installations involving production rates over 900 Mg/h (100 tons/h) have used ball-mill grinding systems. Ring-roll mills are used in smaller applications. Rock for direct use as fertilizer is usually ground to various specifications, ranging from 40 percent minus 200 mesh to 70 percent minus 200 mesh. For manufacture of normal and concentrated superphosphates the fineness of grind ranges from 65 percent minus 200 mesh to 85 percent minus 200 mesh.

Grindability of phosphate rocks from different areas varies widely; in Table 20-31 typical work-index data are shown.

Grinding-media wear in phosphate ball-mill grinding systems ranges from 5 to 25 g/Mg (0.05 to 0.20 lb/ton) ground; ball-mill liners show an average consumption of 2.5 to 100 g/Mg (0.01 to 0.05 lb/ton) ground.

Inorganic salts often do not require fine pulverizing, but they frequently become lumpy. In such cases, they are passed through a double-cage mill or some type of hammer mill.

Basic slag is often used as a source of phosphorus. Its grinding resistance depends largely upon the way in which it has been cooled, slowly cooled slag generally being more easily pulverized. The most common method for grinding basic slag is in a ball mill, followed by a tube mill or a compartment mill. Both systems may be in closed circuit with an air classifier. A 2.1- by 1.5-m (7- by 5-ft) mill, requiring

TABLE 20-29 Selected Standard Sizes of Coarse Aggregate*

Size number	Nominal size, square openings	Amounts finer than each laboratory sieve (square openings), percent by weight														
		4 in	3½ in	3 in	2½ in	2 in	1½ in	1 in	¾ in	½ in	⅜ in	No. 4 (4760 μm)	No. 8 (2380 μm)	No. 16 (1190 μm)	No. 50 (297 μm)	No. 100 (149 μm)
1	3½ to 1½ in.	100	90 to 100	—	25 to 60	—	0 to 15	—	0 to 5							
2	2½ to 1½ in.	—	—	100	90 to 100	35 to 70	0 to 15	—	0 to 5							
3	2 to 1 in.	—	—	—	100	90 to 100	35 to 70	0 to 15	—	0 to 5						
4	1½ to ¾ in.	—	—	—	—	100	90 to 100	20 to 55	0 to 15	—	0 to 5					
5	1 to ½ in.	—	—	—	—	—	100	90 to 100	20 to 55	0 to 10	0 to 5					
6	¾ to ⅜ in.	—	—	—	—	—	—	100	90 to 100	20 to 55	0 to 15	0 to 5				
7	½ in. to No. 4	—	—	—	—	—	—	—	100	90 to 100	40 to 70	0 to 15	0 to 5			
8	⅜ in. to No. 8	—	—	—	—	—	—	—	—	100	85 to 100	10 to 30	0 to 10	0 to 5		
9	No. 4 to No. 16	—	—	—	—	—	—	—	—	—	100	85 to 100	10 to 40	0 to 10	0 to 5	

*ASTM *Standards on Mineral Aggregates and Concrete,* March 1956.

NOTE: To convert inches to centimeters, multiply by 2.54.

TABLE 20-30 Operating Data for Grinding Oyster Shells and Burned Lime in Hammer Mills

Type of mill	Material	Size, in.	Capacity, tons/hr.	Hp.
Jeffrey	Oyster shells	15 × 8	0.5–0.75	8
		20 × 12	1–1.5	12
		24 × 18	2–3	20
		30 × 24	4–5	30
		36 × 24	8–10	40
Stedman	Burned lime	12 × 9	1.5	8
		20 × 12	4	20
		24 × 20	8	40
		30 × 30	12	60
		36 × 36	20	100

NOTE: To convert inches to centimeters, multiply by 2.54; to convert tons per hour to megagrams per hour, multiply by 0.907; and to convert horsepower to kilowatts, multiply by 0.746.

TABLE 20-31 Ball-Mill Grindability of Various Phosphate Rocks

Rock type	Calcium phosphate content, %	Work index, kw.-hr./ton
Central Florida, pebble	68	14.5–16.5
North Florida, pebble	72	18.0–21.0
North Carolina, calcined concentrate	62–67	14.2–18.0
Central Florida, concentrate	72–74	16.0–23.0
Morocco	80–82	10.1–23.6
Idaho		19.0–24.7

NOTE: To convert kilowatthours per ton to kilowatthours per megagram, multiply by 1.1.

94 kW (125 hp), operating with a 4.2-m (14-ft) 22.5-kW (30-hp) classifier, gave a capacity of 4.5 Mg/h (5 tons/h) from the classifier, 95 percent through a No. 200 sieve. Mill product was 68 percent through a No. 200 sieve, and circulating load 100 percent.

CEMENT, LIME, AND GYPSUM

Portland-cement manufacture requires grinding on a very large scale and entails a large use of electric power. Raw materials consist of sources of lime, alumina, and silica and range widely in properties, from crystalline limestone with silica inclusions to wet clay. Therefore a variety of crushers are needed to handle these materials. Typically a crushability test is conducted by measuring the product size from a laboratory impact mill on core samples [Schaefer and Gallus, *Zement-Kalk-Gips,* **41**(10), 486–492 (1988); English ed., 277–280]. Abrasiveness is measured by weight loss of the hammers. The presence of 5 to 10 percent silica can result in an abrasive rock, but only if the silica grain size exceeds 50 μm. Silica inclusions can also occur in soft rocks. The presence of sticky clay will usually result in handling problems, but other rocks can be handled even if moisture reaches 20 percent.

If the rock is abrasive, the first stage of crushing may use gyratory or jaw crushers, otherwise a rotor-impact mill. Their reduction ratio is only 1:12 to 1:18, so they often must be followed by a hammer mill, or they can feed a roll press. Rotor crushers have become the dominant primary crusher for cement plants because of the characteristics. All of these types of crushers may be installed in moveable crusher plants.

In the grinding of raw materials, two processes are used: the dry process in which the materials are dried to less than 1 percent moisture and then ground to a fine powder, and the wet process in which the grinding takes place with addition of water to the mills to produce a slurry. The two processes are used about equally in the United States.

Dry-Process Cement After crushing, the feed may be ground from a size of 5 to 6 cm (2 to 2½ in) to a powder of 75 to 90 percent passing a 200-mesh sieve in one or several stages.

The first stage, reducing the material size to approximately 20 mesh, may be done in vertical, roller, ball-race, or ball mills. The last-named rotate from 15 to 18 r/min and are charged with grinding balls 5 to 13 cm (2 to 5 in) in diameter. The second stage is done in tube mills charged with grinding balls of 2 to 5 cm (¾ to 2 in).

Frequently ball and tube mills are combined into a single machine consisting of two or three compartments, separated by perforated-steel diaphragms and charged with grinding media of different size. Rod mills are hardly ever used in cement plants. The compartments of a tube mill may be combined in various circuit arrangements with classifiers, as shown in Fig. 20-59.

A dry-process plant has been described by Bergstrom [*Rock Prod.,* 59–62 (August 1968)].

Wet-Process Cement Ball, tube, and compartment mills of essentially the same construction as for the dry process are used for grinding. Water or clay slip is added at the feed end of the initial grinder, together with the roughly proportioned amounts of limestone and other components.

In modern installations wet grinding is sometimes accomplished in ball mills alone, operating with excess water in closed circuit with classifiers and hydroseparators.

Figures 20-43 to 20-44 illustrate single-stage and two-stage closed-circuit wet-grinding systems. The circuits of Fig. 20-59 may also be used as a closed-circuit wet-grinding system incorporating a liquid-solid cyclone as the classifier.

A wet-process plant making cement from shale and limestone has been described by Bergstrom [*Rock Prod.,* 64–71 (June 1967)]. There are separate facilities for grinding each type of stone. The ball mill operates in closed circuit with a battery of Dutch State Mines screens. Material passing the screens is 85 percent minus 200 mesh. The entire process is extensively instrumented and controlled by computer. Automatic devices sample crushed rock, slurries, and finished product for chemical analysis by X-ray fluorescence. Mill circuit feed rates and water additions are governed by conventional controllers.

Finish-Grinding of Cement Clinker Typically the hot clinker is first cooled and then ground in a compartment mill in closed circuit with an air classifier. To crush the clinkers, balls as large as 5 in may be needed in the first compartment. A roll press added before the ball mill can reduce clinkers to a fine size, and thus reduce the load on the ball mills. The main reasons for adding a roll press has been to increase capacity of the plant, and lower cost.

Installation of roll presses in several cement plants is described (31st IEEE Cement Industry Technical Conference, 1989). Considerable modification of the installation was required because of the characteristics of the press. A roll press is a constant throughput machine, and the feed rate cannot easily be reduced to match the rate accepted by the ball mill that follows it. Several mills attempted to control the rate by increasing the recycle of coarse rejects from the air classifier, but the addition of such fine material was found to increase the pull-in capacity of the rolls, for example from 180 to 250 t/hr. With the resulting high recycle ratio of 5:1 the roll operation became unstable, and power peaks occurred. Deaeration of fines occurs in the nip, and this also interferes with feeding fines to the rolls. In some plants these problems were overcome by recirculating slabs of product directly from the roll discharge (Fig. 20-26). In other cases the rolls were equipped with variable speed drives to allow more versatile operation when producing several different grades/finenesses of cement. The roll press was found to be 2.5 times as efficient as the ball mill, in terms of new surface per unit energy.

Tests showed that the slab from pressing of clinker at 120 bar and 20 percent recycle contained 97 percent finer than 2.8 mm, and 39

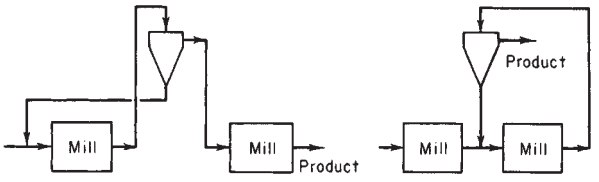


FIG. 20-59 Two cement-milling circuits. [*For others, see Tonry,* Pit Quarry *(February-March 1959).*]

percent finer than 48 μm. Current operation is at 160 bar. The wear was small; after 4000 h operation and 1.5 million tons of throughput the wear rate was less than 0.1 g per ton, or 0.215 g/ton of finished cement. There is some wear of the working parts of the press, requiring occasional maintenance. The press is controlled by four control loops. The main control adjusts the gates that control slab recycle. Since this adjustment is sensitive, the level in the feed bin is controlled by adjusting the clinker-feed rate to assure choke-feed conditions. Hydraulic pressure is also controlled. Separator-reject rate is fixed. The investment cost was only $42,000 per ton of increased capacity. Energy savings is 15 kWh/ton. This together with off-peak power rates results in energy cost savings of $500,000/yr.

Particle-Size Control The strength of cements varies with fineness to which it is ground, and also with size distribution, which affects particle packing. Controlling the particle-size distribution of cements to achieve a higher packing density can give higher strengths, (Helmuth, 23rd IEEE Cement Industry Technical Conference, 1981, 33 pp.). See subsection "Refractories" for further discussion of particle packing.

There have been efforts to take advantage of the greater energy efficiency and lower cost of the roll press for product grinding [Wuestner et al., *Zement-Kalk-Gips,* **41**(7), 345–353 (1987); English ed., 207–212]. However, the much steeper size distribution [Tamashige, *32d IEEE Cement Industry Technical Conference,* 319–340 (1990)], requires a fine size that results in greatly increased water requirement and very rapid setting, which are unacceptable. Also, insufficient heat is generated to dehydrate the gypsum component [Rosemann et al., *Zement-Kalk-Gips,* **42**(4), 165–9 (1987); English ed., 141–3]. It has also been found that the impact deagglomerators tried so far did not completely break up agglomerates as well as a ball mill. Thus there is room for further improvements in developing ways to optimize cement particle-size distribution.

Lime Lime used for agricultural purposes generally is ground in hammer mills. It includes burnt, hydrated, and raw limestone. When a fine product is desired, as in the building trade and for chemical manufacture, ring-roller mills, ball mills, and certain types of hammer mills are used.

Gypsum When gypsum is calcined in rotary kilns, it is first crushed and screened. After calcining it is pulverized. Tube mills are usually used. These impart plasticity and workability. Occasionally such calcined gypsum is passed through ring-roller mills ahead of the tube mills.

COAL, COKE, AND OTHER CARBON PRODUCTS

Bituminous Coal The grinding characteristics of bituminous coal are affected by impurities contained, such as inherent ash, slate, gravel, sand, and sulfur balls. The grindability of coal is determined by grinding it in a standard laboratory mill and comparing the results with the results obtained under identical conditions on a coal selected as a standard. This standard coal is a low-volatile coal from Jerome Mines, Upper Kittaning bed, Somerset County, Pennsylvania, and is assumed to have a grindability of 100. Thus a coal with a grindability of 125 could be pulverized more easily than the standard, while a coal with a grindability of 70 would be more difficult to grind. (Grindability and grindability methods are discussed under "Properties of Solids.")

Anthracite Anthracite is harder to reduce than bituminous coal. It is pulverized for foundry-facing mixtures in ball mills or hammer mills followed by air classifiers. Only to a lesser extent is it used for fuel in powdered form.

A 3- by 1.65-m (10-ft by 66-in) Hardinge mill in closed circuit with an air classifier as shown in Fig. 20-42, grinding 4-mesh anthracite with 3.5 percent moisture, produced 10.8 Mg/h (12 tons/h), 82 percent through No. 200 sieve. The power required for the mill was 278 kW (370 hp); for auxiliaries, 52.5 kW (70 hp); speed of mill, 19 r/min; ball load, 25.7 Mg (28.5 tons). Data for a similar pilot circuit are given in Table 20-32 (Sanner, U.S. Bur. Mines Rep. Invest. 7170, 1968).

Anthracite for use in the manufacture of electrodes is calcined, and the degree of calcination determines the grinding characteristics. Calcined anthracite is generally ground in ball and tube mills or ring-roller mills equipped with air classification. A Raymond high-side ring-roller mill grinding calcined anthracite for electrode manufacture has a capacity of 2.1 Mg/h (4600 lb/h) for a product fineness of 76 percent passing a No. 200 sieve and 52.5-kW (70-hp) power requirement.

TABLE 20-32 Closed-Circuit Continuous Grinding of Anthracite in an Air-Swept Ball Mill

Production rate, lb/h	Mean product size, μm	Circulating load, %	Recirculated material, –37 μm, %	Energy, kWh ton
19.8	7.3	277	42	330
23.0	6.6	283	59	280
27.0	6.1	757	31	246

NOTE: To convert pounds per hour to kilograms per hour, multiply by 0.454; to convert kilowatthours per ton to kilowatthours per megagram, multiply by 1.1.

Coke The grinding characteristics of coke vary widely. By-product coke is hard and abrasive, while certain foundry and retort coke is extremely hard to grind. For certain purposes it may be necessary to produce a uniform granule with minimum fines. This is best accomplished in rod or ball mills in closed circuit with screens. Hourly capacity of a 1.2- by 3-m (4- by 10-ft) rod mill with screens, operating on by-product-coke breeze, was 8.1 Mg (9 tons), 100 percent through No. 10 sieve, and 73 percent on No. 200 sieve; power requirement, 30 kW (40 hp).

Petroleum coke is generally pulverized for the manufacture of electrodes; ring-roller mills with air classification and tube mills are generally used. A No. 5057 Raymond ring-roller mill gave an hourly output of 3.8 tons, 78.5 percent through No. 200 sieve, with 67 kW (90 hp).

Other Carbon Products **Pitch** may be pulverized as a fuel or for other commercial purposes; in the former case the unit system of burning is generally employed, and the same equipment is used as described for coal. Grinding characteristics vary with the melting point, which may be anywhere from 50 to 175°C.

Natural graphite may be divided into three grades in respect to grinding characteristics: flake, crystalline, and amorphous. Flake is generally the most difficult to reduce to fine powder, and the crystalline variety is the most abrasive. Graphite is ground in ball mills, tube mills, ring-roller mills, and jet mills with or without air classification. Beneficiation by flotation is an essential part of most current procedures.

Majac jet-pulverizer performance on natural graphite is given in Table 20-27. Graphite for pencils has 47, 83, 91, and 94 percent by weight smaller than 4, 9, 18, and 31 μm respectively.

Artificial graphite has been ground in ball mills in closed circuit with air classifiers. For lubricants the graphite is ground wet in a paste in which water is eventually replaced by oil. The colloid mill is used for production of graphite paint.

Mineral black, a shale sometimes erroneously called "rotten stone," contains a large amount of carbon and is used as a filler for paints and other chemical operations. It is pulverized and classified with the same equipment as shale, limestone, and barite.

Bone black is sometimes ground very fine for paint, ink, or chemical uses. A tube mill often is used, the mill discharging to a fan which blows the material to a series of cyclone collectors in tandem.

Decolorizing carbons of vegetable origin should not be ground too fine. Standard fineness varies from 100 percent through No. 30 sieve to 100 percent through No. 50, with 50 to 70 percent on No. 200 sieve as the upper limit. Ball mills, hammer mills, and rolls, followed by screens, are used. When the material is used for filtering, a product of uniform size must be used.

Charcoal usually is ground in hammer mills with screen or air classification. For absorption of gases it is usually crushed and graded to about No. 16 sieve size. Care should be taken to prevent it from igniting during grinding.

Gilsonite sometimes is used in place of asphalt or pitch. It is easily pulverized and is generally reduced on hammer mills with air classification.

CHEMICALS, PIGMENTS, AND SOAPS

Colors and Pigments **Dry colors** and **dyestuffs** generally are pulverized in hammer mills (see Table 20-21 or 20-23). The jar mill or

a large pebble mill is often used for small lots. There is a special problem with some dyes which are coarsely crystalline. These are ground to the desired fineness with hammer or jet mills using air classification to limit the size. Synthetic mineral pigments are usually fine agglomerates. They may be disintegrated with hammer or jet mills without elaborate pregrinding. A 1.5- by 0.4-m (4.5-ft by 16-in) Hardinge conical mill in closed circuit with classifier, grinding 50-mesh iron oxide with 33 percent moisture for the paint trade, showed a capacity of 22.5 Mg/day (25 tons/day), 100 percent through No. 200 sieve. Power consumption was 15 kW (20 hp), mill speed 30 r/min, ball load 1800 kg (4000 lb). The conditions necessary for dispersing pigments in paint by means of steel-ball mills have been investigated [Fischer, *Ind. Eng. Chem.*, **33**(12), 1465–1472 (1941)]. Other examples for iron pigments are given in Table 20-33.

Easily dispersible colors are not ordinarily ground fine, since they are subsequently processed in a liquid medium in pebble mills, rolls, or colloid mills. There is, however, a tendency to grind them wet with a dispersing agent, then drying and pulverizing, after which they are easily dispersed in the vehicle in which they are used.

White pigments are the basic commodities processed in large quantities. Titanium dioxide is the most important. The problem of cleaning the mill between batches does not exist as with different colors. These pigments are finish-ground to sell as dry pigments using mills with air classification. For the denser, low-oil-absorption grades, roller and pebble mills are employed. For looser, fluffier products, hammer and jet mills are used. Often a combination of the two mill actions is used to set the finished quality. Jet-mill performance for a number of extenders is given in Table 20-26.

Lead Oxides Leady litharge containing 25 to 30 percent free lead is required for storage-battery plates. It is processed on Raymond Imp mills. They have the ability to produce litharge that has a desired low density of 1.1 to 1.3 g/cm^3 (18 to 22 g/in^3). A 56-kW (75-hp) unit produces 860 kg/h (1900 lb/h) of material having this density.

The processing of **diatomite** is unique, since its particle-size control is effected by calcination treatments and air classification.

Chemicals The fineness obtainable with a hammer mill on rock salt and chemicals is given in Tables 20-23 and 20-24.

Sulfur The ring-roller mill can be used for the fine grinding of sulfur. Inert gases are supplied instead of hot air (see "Properties of Solids: Safety" for use of inert gas). Performance of a Raymond No. 5057 ring-roller mill is given in Table 20-34. The total cost might be 3 to 4 times the power cost and include labor, inert gas, maintenance, and fixed charges.

Soaps Soaps in a finely divided form may be classified as soap powder, powdered soap, and chips or flakes. The term "soap powder" is applied to a granular product, No. 12 to No. 16 sieve size with a certain amount of fines, which is produced in hammer mills with perforated or slotted screens.

The oleates and erucates are best pulverized by multicage mills; laurates and palmitates, in cage mills and also in hammer mills if particularly fine division is not required; stearates may generally be pulverized in multicage mills, screen mills, and air-classification hammer mills.

TABLE 20-33 Grinding Iron Oxides in a Ring-Roller Mill

Material	Fineness	Capacity, lb./hr.	Total hp.-hr./ton
Raw sienna	99% through No. 200 sieve	5950	23.5
Burnt sienna	99.5% through No. 200 sieve	5800	22.1
Raw umber	99% through No. 200 sieve	5200	26.9
Burnt umber	99.5% through No. 200 sieve	5400	25.9
Natural ocher	99.9% through No. 200 sieve	4500	31.0
Iron oxide (ore)	99% through No. 325 sieve	3100	45.0
Iron oxide (precipitated)	99.9% through No. 325 sieve	1800	72.5

NOTE: To convert pounds per hour to kilograms per hour, multiply by 0.4535; to convert horsepower-hours per ton to kilowatthours per megagram, multiply by 0.82.

TABLE 20-34 Grinding Sulfur

Fineness, % through No. 325 sieve	Capacity, tons/hr.	Power, kw.-hr./ton
90	6.0	13.7
95	5.0	16.4
99	3.5	23.4
99.9	2.5	32.7

NOTE: To convert tons per hour to megagrams per hour, multiply by 0.907; to convert kilowatthours per ton to kilowatthours per megagram, multiply by 1.1.

ORGANIC POLYMERS

The grinding characteristics of various resins, gums, waxes, hard rubbers, and molding powders depend greatly upon their softening temperatures. When a finely divided product is required, it is often necessary to use a water-jacketed mill or a pulverizer with an air classifier in which cooled air is introduced into the system. Hammer and cage mills are used for this purpose. Some low-softening-temperature resins can be ground by mixing with 15 to 50 percent by weight of dry ice before grinding. Refrigerated air sometimes is introduced into the hammer mill to prevent softening and agglomeration [Dorris, *Chem. Metall. Eng.*, **51,** 114 (July 1944)].

Most **gums and resins,** natural or artificial, when used in the paint, varnish, or plastic industries, are not ground very fine, and hammer or cage mills will produce a suitable product. Typical performance of the disk attrition mill is given in Table 20-25. Roll crushers will often give a sufficiently fine product.

The Raymond ring-roll mill with its internal air separation is widely used to pulverize **phenolformaldehyde resins.** The usual fineness of grind is finer than 99 percent minus 200 mesh. Air at 4°C (40°F) is usually introduced into the mill to limit temperature rise. A typical 3036 Raymond mill using 34 kW (45 hp) will produce better than 900 kg/h (2000 lb/h) at 99 percent minus 200 mesh.

Hard rubber is one of the few combustible materials which is generally ground on heavy steam-heated rollers. The raw material passes to a series of rolls in closed circuit with screens and air classifiers. Farrel-Birmingham rolls are used extensively for this work. There is a differential in the roll diameters. The motor should be separated from the grinder by a fire wall.

Specifications for **molding powders** vary widely, from a No. 8 to a No. 60 sieve product; generally the coarser products are No. 12, 14, or 20 sieve material. Specifications usually prescribe a minimum of fines (below No. 100 and No. 200 sieve). Molding powders are produced with hammer mills, either of the screen type or equipped with air classifiers.

The following materials may be ground at ordinary temperatures if only the regular commercial fineness is required: amber, arabac, tragacanth, rosin, olibanum, gum benzoin, myrrh, guaiacum, and montan wax. If a finer product is required, hammer mills or attrition mills in closed circuit, with screens or air classifiers, are used.

PROCESSING WASTE

In flowsheets for processing *municipal solid waste* (MSW), the objective is to separate the waste into useful materials, such as scrap metals, plastics, and *refuse-derived fuels* (RDF). Usually size reduction is the first step, followed by separations with screens or air classifiers, which attempt to recover concentrated fractions [Savage and Diaz, *Proceedings ASME National Waste Processing Conference,* Denver, Colo, 361–373 (1986)]. Many installed circuits proved to be ineffective or not cost-effective, however. Begnaud and Noyon [*Biocycle,* **30**(3), 40–41 (1989)] concluded from a study of French operations that milling could not grind selectively enough to separate different materials.

Size reduction uses either hammer mills or blade cutters (shredders). Hammer mills are likely to break glass into finer sizes making it hard to separate. Better results may be obtained in a flowsheet where size reduction follows separation (Savage, Seminar on the Application

of U.S. Water and Air Pollution Control Technology to Korea, Korea, May 1989).

The energy requirement for reducing MSW to 90 percent passing 10 cm is typically 6 kWh/ton, or 50 kWh/ton for passing 1 cm. Wear is also a major cost, and wear rates are shown in Fig. 20-60. The maximum capacity of commercially available hammer mills is about 100 ton/h.

CRYOGENIC GRINDING

This is a process used for recovering recycled materials [Biddulph, *Chemical Engineering,* **87**(3), 93–96 (1980)]. This process permits efficient separation of materials in cases where some materials in a mixture become brittle, while others do not, and it also reduces crusher energy requirements. Examples are rubber crumb recovered in a pure state from scrap tires, which has found uses including road and sports surfaces and polymer fillers. Stripping of polymeric insulation from copper wires occurs when the chilled material is passed through crushing rolls. The Inchscrap process shreds chilled baled automobiles, magnetically separating pure steel and other components. Biddulph (loc. cit.) presents graphs for design of a heat-transfer tunnel using liquid nitrogen. Countercurrent flow of the gas also extracts the latent heat of the nitrogen. The process can be economic where the added value of the recovered product ranges from a few cents to 15 cents/kg.

Results for cryogrinding of polymers in an opposed-jet laboratory mill are given by [Haesse, *Kunststoffe-German Plastics,* **70**(12), 9–10 (1980)].

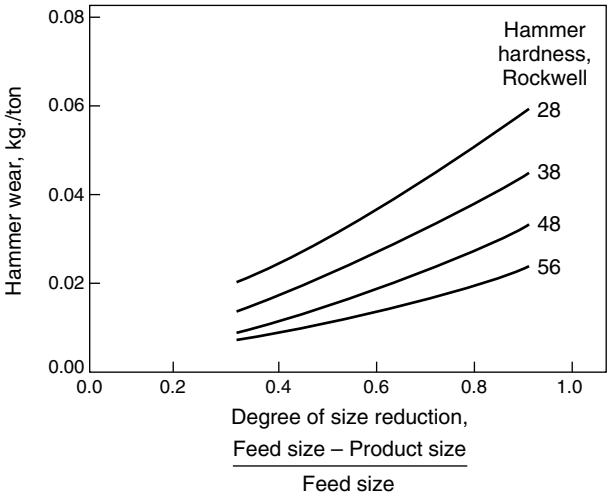


FIG. 20-60 Hammer wear as a consequence of shredding municipal solid waste. (*Savage and Diaz, Proceedings ASME National Waste Processing Conference, Denver, CO, 361–373, 1986.*)

CELL DISRUPTION

Mechanical disruption is the most practical first step in the release and isolation of proteins and enzymes from microorganisms on a commercial scale. The size-reduction method must be gently tuned to the strength of the organisms to minimize formation of fine fragments that interfere with subsequent clarification by centrifugation or filtration. Typically, fragments as fine as 0.3 μm are produced. High-speed stirred-bead mills and high-pressure homogenizers have been applied for cell disruption [Kula and Schuette, *Biotechnology Progress,* **3**(1), 31–42 (1987)].

There are two limiting cases in operation of bead mills for disruption of bacterial cells. When the energy imparted by collision of beads is insufficient to break all cells, the rate of breakage is proportional to the specific energy imparted [Bunge et al., *Chemical Engineering Science,* **47**(1), 225–232 (1992)]. On the other hand, when the energy is high due to higher speed above 8 m/sec, larger beads above 1 mm, and low concentrations of 10 percent, each bead impact has more than enough energy to break any cells that are captured, which causes problems during subsequent separations.

The strength of cell walls differs among bacteria, yeasts, and molds. The strength also varies with the species and the growth conditions, and must be determined experimentally. Beads of 0.5 mm are typically used for yeast and bacteria. Recommended bead charge is 85 percent for 0.5 mm beads, and 80 percent for 1 mm beads [Schuette et al., *Enzyme Microbial Technology,* **5,** 143 (1983)].

Residence-time distribution is important in continuous mills. Further data are given in the above references.

While the above discussion centered on the rate of disruption, the objective is usually to attain at least 90 percent release of the valuable protein from the cells. Cell disruption with protein solubilization is considered to be first order in amount of protein remaining [Currie et al., *Biotechnol. Bioeng.,* **14,** 725 (1972)]:

$$(R_m - R)/R_m = \exp(-kt)$$

where R is residual protein, and R_m is maximum protein removable.

Valve homogenizers have been used to disrupt cells and release soluble components (Pandolf, *Cell Disruption by Homogenization,* APV Gaulin, 1993). The cell disruption is believed due to the sudden pressure drop, although impact may also be a cause [Brookman, *Biotechnol. Bioeng.,* **16,** 371 (1974); Engler and Robinson, *Biotechnol. Bioeng.,* **23,** 765 (1981)]. The release of glycose-6-phosphate dehydrogenase from Saccharomyces cerevisiae is linear with pressure beginning at 200 bar and reaches 40 percent at 550 bar in the Gaulin M3 unit.

PRINCIPLES OF SIZE ENLARGEMENT

GENERAL REFERENCES: Ennis & Litster, *The Science & Engineering of Granulation Processes,* Blackie Academic Ltd., 1997. Ennis (ed.), *Proceedings of the First International Particle Technology Forum, Vol. 1,* AIChE, Denver, 1994. Ennis, *Powder Technology,* **88,** 203 (1996). Kapur, *Adv. Chem. Eng.,* **10,** 55, 1978. Kristensen, *Acta Pharm. Suec.,* **25,** 187, 1988. Pietsch, *Size Enlargement by Agglomeration,* John Wiley & Sons Ltd., Chichester, 1992. Randolph & Larson, *Theory of Particulate Processes,* Academic Press, Inc., San Diego, 1988. Stanley-Wood, *Enlargement and Compaction of Particulate Solids,* Butterworth & Co. Ltd., 1983. Ball et al., *Agglomeration of Iron Ores,* Heinemann, London, 1973. Capes, *Particle Size Enlargement,* Elsevier, New York, 1980. King, "Tablets, Capsules and Pills," in *Remington's Pharmaceutical Sciences,* Mack Pub. Co., Easton, Pa., 1970. Knepper (ed.), *Agglomeration,* Interscience, New York, 1962. Mead (ed.), *Encyclopedia of Chemical Process Equipment,* Reinhold, New York, 1964. Pietsch, *Roll Pressing,* Heyden, London, 1976. Sastry (ed.), *Agglomeration 77,* AIME, New York, 1977. Sauchelli (ed.), *Chemistry and Technology of Fertilizers,* Reinhold, New York, 1960. Sherrington and Oliver, *Granulation,* Heyden, London, 1981.

SCOPE AND APPLICATIONS

Size enlargement is any process whereby small particles are gathered into larger, relatively permanent masses in which the original particles can still be distinguished. The term encompasses a variety of unit-operations or processing techniques dedicated to particle agglomeration. **Agglomeration** is the formation of aggregates through the sticking together of feed and/or recycle material. These processes can be loosely broken down into **agitation** and **compression** methods. Although terminology is industry specific, agglomeration by agitation will be referred to as **granulation.** Here, a particulate feed is

introduced to a process vessel and is agglomerated, either batchwise and continuously, to form a granulated product. Agitative processes include fluid-bed, pan (or disc), drum, and mixer granulators. The feed typically consists of a mixture of solid ingredients, referred to as a **formulation,** which includes an active or key ingredient, binders, diluents, flow aids, surfactants, wetting agents, lubricants, fillers, or end-use aids (e.g., sintering aids, colors or dyes, taste modifiers). The agglomeration can be induced in several ways. A solvent or slurry can be atomized onto the bed of particles which either coats the particle or granule surfaces promoting agglomeration, or the spray drops can form small nuclei in the case of a powder feed which subsequently can agglomerate. The solvent or slurry may contain a binder, or solid binder may be present as one component of the feed. Alternatively, the solvent may induce dissolution and recrystallization in the case of soluble particles. Slurries often contain the same particulate matter as the dry feed, and granules may be formed, either completely or partially, as the droplets solidify in flight prior to reaching the particle bed. **Spray-drying** is an extreme case with no further, intended agglomeration taking place after granule formation. Agglomeration may also be induced by heat, which either leads to controlled **sintering** of the particle bed or induces sintering or partial melting of a binder component of the feed, e.g., a polymer.

An alternative approach to size enlargement is by **compression agglomeration,** where the mixture of particulate matter is fed to a compression device which promotes agglomeration due to pressure. Either continuous sheets of solid material are produced or some solid form such as a **briquette** or **tablet.** Heat or cooling may be applied, and reaction may be induced as for example with sintering. Carrier fluids may be present, either added or induced by melting, in which case the product is **wet extruded.** Continuous compaction processes include roll presses, briquetting machines, and extrusion, whereas batch-like processes include tableting. Some processes operate in a semicontinuous fashion, such as ram extrusion.

At the level of a manufacturing plant, the size-enlargement process involves several peripheral, unit operations such as milling, blending, drying or cooling, and classification, referred to generically as an **agglomeration circuit** (Fig. 20-61). In addition, more than one agglomeration step may be present as in the case of a pharmaceutical process which often involves both an agitative-granulation technique followed by the compressive technique of tableting.

Numerous benefits result from size-enlargement processes, as will be appreciated from Table 20-35. A wide variety of size-enlargement methods are available; a classification of these is given in Table 20-36.

APPROACHING THE DESIGN OF SIZE-ENLARGEMENT PROCESSES

Agglomeration Kinetics A change in particle size of a particulate material due to agglomeration is akin to a change in chemical species, and so analogies exist between agglomeration and chemical kinetics and the unit operations of size enlargement and chemical reaction. The performance of a **granulator** or **compactor** may be described by the **extent of agglomeration** of a species, typically represented by a loss in number of particles. Let $(x_1, x_2, \ldots, x_n)$ represent a list of attributes such as average particle size, porosity, strength, surface properties, and any generic quality metric and associated variances. Alternatively, $(x_1, x_2, \ldots, x_n)$ might represent the concentrations or numbers of certain size or density classes, just as in the case of chemical reactors. The proper design of a chemical reactor or an **agglomerator** then relies on understanding and controlling the evolution (both time and spatial) of the feed vector **X** to the desired product vector **Y.** Inevitably, the reactor or granulator is contained within a larger plant-scale process chain, or **manufacturing circuit,** with overall plant performance being dictated by the interactions between individual unit operations. For successful plant design and operation, there are four natural levels of scrutiny (Fig. 20-62). Conceptually, the design of chemical reactors and agglomeration processes differ in that the former deals with chemical transformations whereas the latter deals primarily with **physical transformations** with the mechanisms or rate processes of agglomeration controlled by a set of key **physicochemical interactions.**

Granulation Rate Processes Granulation is controlled by four key rate processes. These include wetting, coalescence or growth, consolidation, and breakage (Fig. 20-63). Initial **wetting** of the particles by the binding fluid is strongly influenced by spray or fluid distri-

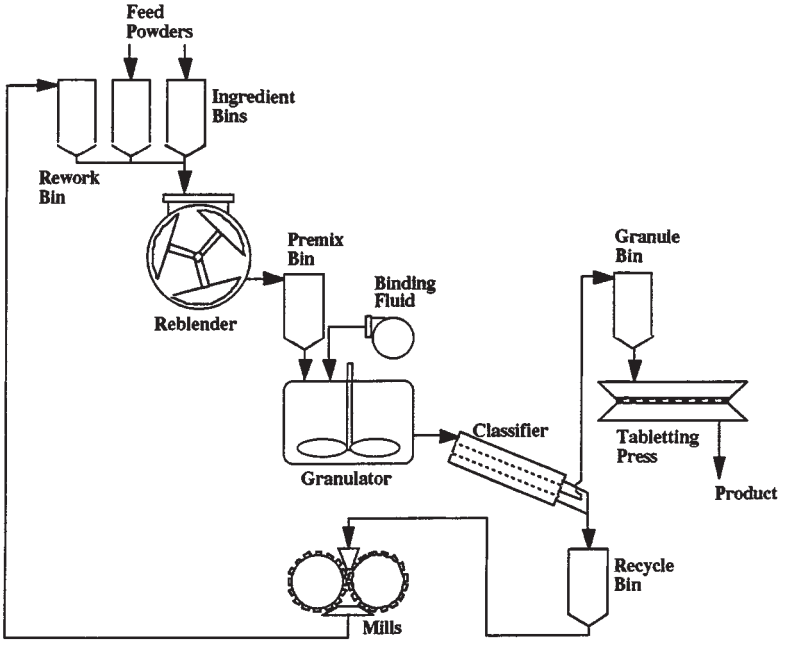


FIG. 20-61 A typical agglomeration circuit utilized in the processing of pharmaceutical or agricultural chemicals involving both granulation and compression techniques. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries,* Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

TABLE 20-35 Objectives of Size Enlargement

Production of useful structural forms, as in pressing of intricate shapes in powder metallurgy.
Provision of a defined quantity for dispensing and metering, as in agricultural chemical granules or pharmaceutical tablets.
Elimination of dust handling hazards or losses, as in briquetting of waste fines.
Improved product appearance, or product renewal.
Reduced caking and lump formation, as in granulation of fertilizer.
Improved flow properties, as in granulation of pharmaceuticals for tabletting or ceramics for pressing.
Increased bulk density for storage.
Creation of non-segregating blends of powder ingredients, as in sintering of fines for steel or agricultural chemical granules.
Control of solubility, as in instant food products.
Control of porosity and surface-to-volume ratio, as with catalyst supports.
Improvement of heat transfer characteristics, as in ores or glass for furnace feed.
Removal of particles from liquid, as with polymer additives which induce clay flocculation.

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bution as well as feed-formulation properties. Often wetting agents such as surfactants are carefully chosen to enhance poorly wetting feeds. In the **coalescence** or **growth** stage, partially wetted primary particles and larger nuclei coalesce to form granules composed of several particles. The term **nucleation** is typically applied to the initial coalescence of primary particles in the immediate vicinity of the larger-wetting drop, whereas the more general term of **coalescence** refers to the successful collision of two granules to form a new larger granule. Nucleation is promoted from some initial distribution of moisture, such as a drop or from the homogenization of a fluid feed to the bed, as with high-shear mixing. The nucleation process is strongly linked with the wetting stage. As granules grow, they become consolidated by the compaction forces of the bed due to agitation. This **consolidation** stage strongly influences final granule porosity, and therefore end-use properties such as granule strength or dispersability. Formed granules may be particularly susceptible to **breakage** if they are inherently weak or if flaws develop during drying. The final size distribution and other end-use properties of the product are determined by the complex interaction of all these rate processes acting simultaneously.

Compaction Rate Processes The performance of compaction techniques is controlled by the ability of the particulate phase to uniformly transmit stress and the relationship between applied stress and the compaction and strength characteristics of the final compacted particulate phase. The general area of study relating compaction and stress transmission is referred to as **powder mechanics** (Brown & Richards, *Principles of Powder Mechanics,* Pergamon Press Ltd., Oxford, 1970).

Process versus Formulation Design The end-use properties of the agglomerated material are controlled by agglomerate size and porosity. Granule structure may also influence properties. To achieve a desired **product quality** as defined by metrics of end-use properties, size and porosity may be manipulated by changes in either process **operating** or product **material variables** (Fig. 20-63). The first approach is the realm of traditional **process engineering,** whereas the second is **product engineering.** Both approaches are

TABLE 20-36 Size-Enlargement Methods and Application

Method	Product size (mm)	Granule density	Scale of operation	Additional comments	Typical applications
Tumbling granulators	0.5 to 20	Moderate	0.5–800 ton/hr	Very spherical granules	Fertilizers, iron ore, non-ferrous ore, agricultural chemicals
Drums					
Discs					
Mixer granulators					
Continuous high shear (e.g. Shugi mixer)	0.1 to 2	Low to high	Up to 50 ton/hr	Handles very cohesive materials well, both batch and continuous	Chemicals, detergents, clays, carbon black
Batch high shear (e.g. paddle mixer)	0.1 to 2	High	Up to 500 kg batch		Pharmaceuticals, ceramics
Fluidized granulators				Flexible, relatively easy to scale, difficult for cohesive powders, good for coating applications	Continuous: fertilizers, inorganic salts, detergents
Fluidized beds	0.1 to 2	Low (agglomerated)	100–900 kg batch		
Spouted beds		Moderate (layered)	50 ton/hr continuous		Batch: pharmaceuticals, agricultural chemicals, nuclear wastes
Wurster coaters					
Centrifugal granulators	0.3 to 3	Moderate to high	Up to 200 kg batch	Powder layering and coating applications	Pharmaceuticals, agricultural chemicals
Spray methods					
Spray drying	0.05 to 0.5	Low		Morphology of spray dried powders can vary widely	Instant foods, dyes, detergents, ceramics
Prilling	0.7 to 2	Moderate			Urea, ammonium nitrate
Pressure compaction		High to very high		Very narrow size distributions, very sensitive to powder flow and mechanical properties	Pharmaceuticals, catalysts, inorganic chemicals, organic chemicals, plastic preforms, metal parts, ceramics, clays, minerals, animal feeds
Extrusion	>0.5		Up to 5 ton/hr		
Roll press	>1		Up to 50 ton/hr		
Tablet press	10		Up to 1 ton/hr		
Molding press					
Pellet mill					
Thermal processes					
Sintering	2 to 50	High to very high	Up to 100 ton/hr	Strongest bonding	Ferrous & non-ferrous ores, cement clinker, minerals, ceramics
Liquid systems					
Immiscible wetting in mixers	<0.3	Low	Up to 10 ton/hr	Wet processing based on flocculation properties of particulate feed	Coal fines, soot and oil removal from water
Sol-gel processes					Metal dicarbide, silica hydrogels
Pellet flocculation					Waste sludges and slurries

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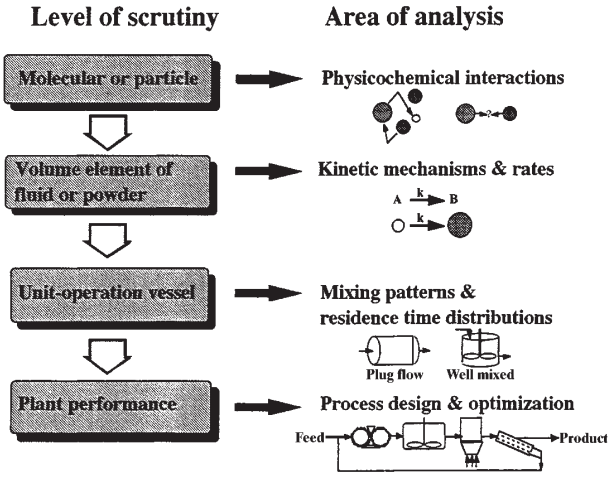


FIG. 20-62 Comparisons of levels of analysis of chemical reaction and size-enlargement processes. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries,* Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

critical and must be integrated to achieve a desired end point in product quality. Operating variables are defined by the chosen agglomeration technique and peripheral processing equipment. In addition, the choice of agglomeration technique dictates the mixing pattern of the vessel. Material variables include parameters such as binder viscosity, surface tension, particle-size distribution and friction, and the adhesive properties of the solidified binder. Material variables are specified by the choice of ingredients, or **product formulation.** Both operating and material variables together define the kinetic mechanisms and rate constants of wetting, growth, consolidation, attrition, and powder flow. Overcoming a given size-enlargement problem often requires changes in both processing conditions and in product formulation.

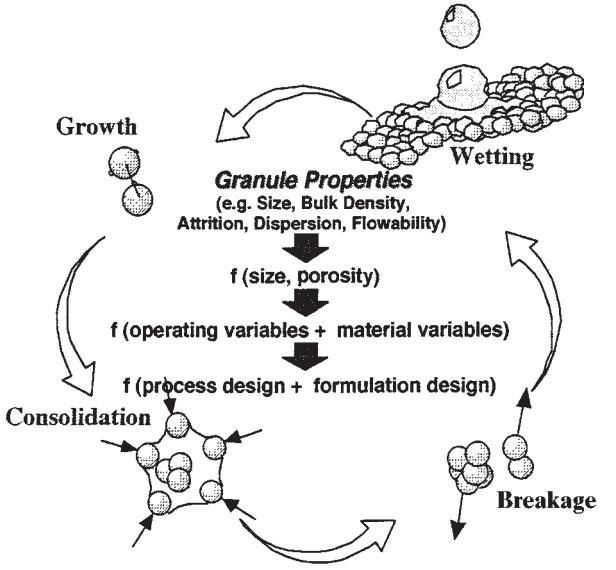


FIG. 20-63 The rate processes of agitative agglomeration, or granulation, which include powder wetting, granule growth, granule consolidation, and granule attrition. These processes combined control granule size and porosity, and they may be influenced by formulation or process-design changes. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries,* Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

PRODUCT CHARACTERIZATION

Powders are agglomerated to modify physical or physicochemical properties. Effective measurement of agglomerate properties is vital. However, many tests are industry specific and take the form of empirical indices based on standardized protocols. Such tests as described below are useful for quality control if used with care. However, since they often reflect an end use rather than a specifically defined agglomerate property, they often are of little developmental utility for recommending process or formulation changes. Significant improvements have been made in the ability to measure real agglomerate properties. Key agglomerate properties are **size, porosity,** and **strength** and their associated distributions. These properties directly affect end-use attributes of the product such as attrition resistance, flowability, bulk-solid permeability, wettability and dispersibility, appearance, or active-agent release rate.

Size Agglomerate **mean size** and **size distribution** are both important properties. (See subsection "Particle-Size Measurement".) For granular materials, sieve analysis is the most common sizing technique. Care is needed in sizing wet granules. Handling during sampling and sieving can cause changes to the size distribution through coalescence or breakage. Sieves are also easily blinded. Snap freezing the granules with liquid nitrogen prior to sizing overcomes these problems [Hall, *Chem. Eng. Sci.,* **41,** 187 (1986)]. On-line or in-line measurement of granules as large as 9 mm is now available by laser diffraction techniques, making improved granulation control schemes possible [Ogunnaike et al., *I.E.C. Fund.,* 1997].

Porosity and Density There are three important densities of granular or agglomerated materials: **bulk density** ρ_b (related to the volume occupied by the bulk solid), the apparent or **agglomerate density** ρ_g (related to the volume occupied by the agglomerate including internal porosity) and the true or **skeletal-solids density** ρ_s. These densities are related to the each other and the interagglomerate **voidage** ε_b and the intra-agglomerate **porosity** ε_g:

$$\varepsilon_b = 1 - \frac{\rho_b}{\rho_a};\ \varepsilon_g = 1 - \frac{\rho_a}{\rho_s} \qquad (20\text{-}42)$$

Bulk density is easily measured from the volume occupied by the bulk solid and is a strong function of sample preparation. True density is measured by standard techniques using liquid or gas picnometry. Apparent (agglomerate) density is difficult to measure directly. Hinkley et al. [*Int. J. Min. Proc.,* **41,** 53–69 (1994)] describe a method for measuring the apparent density of wet granules by kerosene displacement. Agglomerate density may also be inferred from direct measurement of true density and porosity using Eq. (20-42).

Agglomerate porosity can be measured by gas adsorption or mercury porosimetry. However, any breakage or compression of the granules under high pressure during porosimetry can invalidate the results.

Strength of Agglomerates **Agglomerate bonding mechanisms** may be divided into five major groups [Rumpf, in Knepper (ed.), *Agglomeration,* op. cit., p. 379]. More than one mechanism may apply during a given size-enlargement operation. (In addition, see Krupp [*Adv. Colloid. Int. Sci.,* **1,** 111 (1967)] for a review of adhesion mechanisms.)

Solid bridges can form between particles by the sintering of ores, the crystallization of dissolved substances during drying as in the granulation of fertilizers, and the hardening of bonding agents such as glue and resins.

Mobile liquid binding produces cohesion through interfacial forces and capillary suction. Three states can be distinguished in an assembly of particles held together by a mobile liquid (Fig. 20-64). Small amounts of liquid are held as discrete lens-shaped rings at the points of contact of the particles; this is the **pendular state.** As the liquid content increases, the rings coalesce and there is a continuous network of liquid interspersed with air; this is the **funicular state.** When all the pore spaces in the agglomerate are completely filled, the **capillary state** has been reached. When a mobile liquid bridge fails, it con-



FIG. 20-64 Three states of liquid content for an assembly of spherical particles. (*a*) Pendular state. (*b*) Funicular state. (*c*) Capillary state. [*Newitt and Conway-Jones,* Trans. Inst. Chem. Eng. (London), **36,** *422 (1958).*]

stricts and divides without fully exploiting the adhesion and cohesive forces in the bridge in the absence of viscous effects. Binder viscosity markedly increases the strength of the pendular bridge due to dynamic lubrication forces, and aids the transmission of adhesion. For many systems, viscous forces outweigh interfacial capillary effects, as demonstrated by Ennis et al. [*Chem. Eng. Sci.,* **45,** 3071 (1990)].

In the limit of high viscosity, **immobile liquid bridges** formed from materials such as asphalt or pitch fail by tearing apart the weakest bond. Then adhesion and/or cohesion forces are fully exploited, and binding ability is much larger.

Intermolecular and **electrostatic forces** bond very fine particles without the presence of material bridges. Such bonding is responsible for the tendency of particles less than about 1 μm diameter to form agglomerates spontaneously under agitation. With larger particles, however, these short-range forces are insufficient to counterbalance the weight of the particle, and adhesion does not occur without applied pressure. High compaction pressures act to plastically flatten interparticle contacts and substantially enhance short-range forces.

Mechanical interlocking of particles may occur during the agitation or compression of, for example, fibrous particles, but it is probably only a minor contributor to agglomerate strength in most cases.

For an agglomerate of equal-sized spherical particles (Rumpf, loc. cit., 379), the tensile strength is

$$\sigma_T = \frac{9}{8}\,\frac{1-\varepsilon_g}{\varepsilon_g}\,\frac{H}{d^2} \qquad (20\text{-}43)$$

where H is the individual bonding force per point of contact and d is the size of particles making up the granule. For other bonding mechanisms, Fig. 20-65 indicates values of tensile strength to be expected in various size enlargement processes. In particular, it should be noted that viscous mechanisms of binding (e.g., adhesives) can exceed capillary effects in determining agglomerate strength.

Strength Testing Methods Compressed agglomerates often fail in **tension** along their diameter. This is the basis of the commonly used measurement of **crushing strength** of a agglomerate as a method to assess tensile strength. However, the brittle failure of a granule depends on the flaw distribution as well as the inherent tensile strength of bonds as given by the Griffith crack theory. [Lawn, *Fracture of Brittle Solids,* 2d ed., Cambridge University Press, 1975] Therefore, it is more appropriate to characterize granule strength by **fracture toughness** K_c [Kendall, *Nature,* **272,** 710 (1978); See also subsections "Size Reduction: Properties of Solids" and "Breakage"].

Several strength-related indices are measured in different industries which give some measure of resistance to attrition. These tests do not measure strength or toughness directly, but rather the size distribution of fragments after handling the agglomerates in a defined way. The handling could be repeated drops, tumbling in a drum, fluidizing, circulating in a pneumatic conveying loop, etc. These indices should only be used for quality control if the test procedure simulates the actual handling of the agglomerates during processing and transportation.

Flow Property Tests **Flowability** of the product granules can be characterized by **unconfined yield stress** and **angle of friction** by

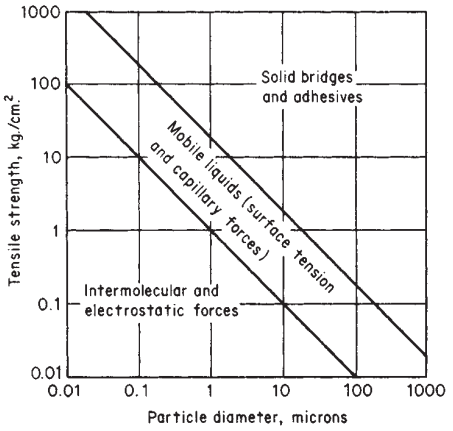


FIG. 20-65 Theoretical tensile strength of agglomerates. [*Adapted from Rumpf, "Strength of Granules and Agglomerates," in Knepper (ed.),* Agglomeration, *Wiley, New York, 1962.*]

shear-cell tests as used generally for bulk solids (see subsection "Powder Mechanics and Powder Compaction" and also Section 21, Solids Transport and Storage). **Caking** refers to deterioration in the flow properties of the granules due to chemical reaction or hydroscopic effects. Caking tests as used for fertilizer granules consist of two parts (Bookey and Raistrick, in Sauchelli (ed.), *Chemistry and Technology of Fertilizers,* p. 454). A cake of the granules is first formed in a compression chamber under controlled conditions of humidity, temperature, etc. The crushing strength of the cake is then measured to determine the degree of caking.

Redispersion Tests Agglomerated products are often **redispersed** in a fluid by a customer. Examples include the dispersion of fertilizer granules in spray-tank solutions or of tablets within the gastrointestinal tract of the human body. The mechanisms comprising this redispersion process of product **wetting,** agglomerate **disintegration,** and final **dispersion** are related to interfacial properties (For details, see subsection "Wetting"). There are a wide range of industry-specific empirical indices dealing with redispersion assessment.

Disintegration height tests consist of measuring the length required for complete agglomerate disintegration in a long, narrow tube. Small fragments may still remain after initial agglomerate disintegration. The residual of material which remains undispersed is measured by a related test, or **long-tube sedimentation test.** The residual undispersed material is reported by the level in the bottom tip of the tube. A variation of this test is the **wet screen test,** which measures the residual remaining on a fine mesh screen (e.g., 350 mesh) following pouring the beaker solution through the screen.

Tablet-disintegration tests consist of cyclical immersion in a suitable dissolving fluid of pharmaceutical tablets contained in a basket. Acceptable tablets disintegrate completely by the end of the specified test period (*United States Pharmacopeia,* 17th rev., Mack Pub. Co., Easton, Pa., 1965, p. 919).

Permeability **Bulk solid permeability** is important in the iron and steel industry where gas-solid reactions occur in the sinter plant and blast furnace. It also strongly influences compaction processes where entrapped gas can impede compaction, and solids-handling equipment where restricted gas flow can impede product flowability. The permeability of a granular bed is inferred from measured pressure drop under controlled gas-flow conditions.

AGGLOMERATION RATE PROCESSES

General References: Adetayo *et al., Powder Tech.,* **82,** 37 (1995). Brown & Richards, *Principles of Powder Mechanics,* Pergamon Press (1970). Carson & Marinelli, *Chemical Eng.,* April (1994). Ennis & Litster, *The Science & Engineering of Granulation Processes,* Blackie Academic Ltd., 1997. Ennis *et al., Powder Tech.,* **65,** 257 (1991). Ennis & Sunshine, *Tribology International,* **26,** 319 (1993). Ennis (ed.), *Proceedings of the First International Particle Technology Forum, Vol. 1,* AIChE, Denver, 1994. Ennis, *Powder Technology,* **88,** 203 (1996). Kristensen, *Acta Pharm. Suec.,* **25,** 187, 1988. Lawn, *Fracture of Brittle Solids,* 2nd ed., Cambridge University Press, 1975. Owens & Wendt, *J. Appl. Polym. Sci.,* **13,** 1741 (1969). Pan *et al., Dynamic Properties of Interfaces & Association Structure,* American Oil Chem. Soc. Press (1995). Parfitt (ed.), *Dispersion of Powders in Liquids,* Elsevier Applied Science Publishers Ltd., 1986.

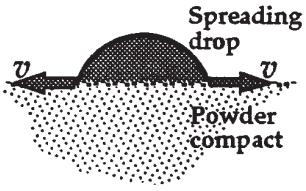
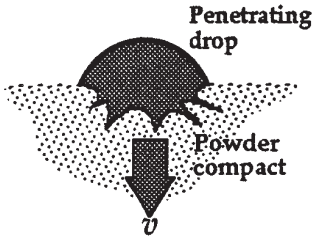
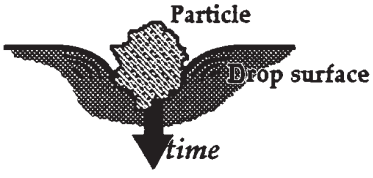
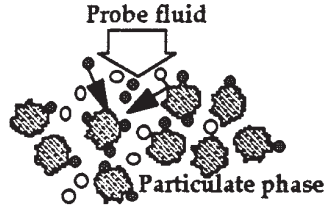
WETTING

The initial distribution of binding fluid can have a pronounced influence on the size distribution of seed granules, or **nuclei,** which are formed from fine powder. Both the final **extent** of and the **rate** at which the fluid wets the particulate phase are important. For a poor wetting fluid, a substantial portion of the powder remains ungranulated. When the size of a particulate feed material is larger than drop size, wetting dynamics controls the distribution of coating material which has a strong influence on the later stages of growth. Wetting phenomena also influence redistribution of individual ingredients within a granule, drying processes, and redispersion of granules in a fluid phase (e.g., agricultural chemicals and pharmaceutical products).

Methods of Measurement Methods of characterizing the rate process of wetting include four approaches as illustrated in Table 20-37. The first considers the ability of a drop to spread across the powder. This approach involves the measurement of a **contact angle** of a drop on a powder compact. The contact angle is a measure of the affinity of the fluid for the solid as given by the Young-Dupré equation, or

$$\gamma^{sv} - \gamma^{sl} = \gamma^{lv} \cos \theta \qquad (20\text{-}44)$$

TABLE 20-37 Methods of Characterizing Wetting Dynamics of Particulate Systems*

Mechanism of wetting	Characterization method
Spreading of drops on powder surface 	**Contact angle goniometer** Contact angle Drop height or volume Spreading velocity **References:** Kossen & Heertjes, *Chem. Eng. Sci.,* **20,** 593 (1965). Pan et al., *Dynamic Properties of Interfaces & Association Structure,* American Oil Chem. Soc. Press (1995)
Penetration of drops into powder bed 	**Washburn test** Rate of penetration by height or volume **Bartell cell** Capillary pressure difference **References:** Parfitt (ed.), *Dispersion of Powders in Liquids,* Elsevier Applied Science Publishers Ltd., 1986. Washburn, *Phys. Rev.,* **17,** 273 (1921). Bartell & Osterhof, *Ind. Eng. Chem.,* **19,** 1277 (1927).
Penetration of particles into fluid 	**Flotation tests** Penetration time Sediment height Critical solid surface energy distribution **References:** R. Ayala, Ph.D. Thesis, Chem. Eng., Carnegie Mellon Univ. (1985). Fuerstaneau et al., *Colloids & Surfaces,* **60,** 127 (1991). Vargha-Butler, et al., *Colloids & Surfaces,* **24,** 315 (1987).
Chemical probing of powder 	**Inverse gas chromatography** Preferential adsorption with probe gases **Electrokinetics** Zeta potential and charge **Surfactant adsorption** Preferential adsorption with probe surfactants **References:** Lloyd et al. (eds.), ACS Symposium Series **391,** ACS, Washington D.C. (1989). Aveyard & Haydon, *An Introduction to the Principles of Surface Chemistry,* Cambridge Univ. Press (1973). Shaw, *Introduction to Colloid & Surface Chemistry,* Butterworths & Co. Ltd. (1983).

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where γ^{sv}, γ^{sl}, γ^{lv} are the solid-vapor, solid-liquid, and liquid-vapor interfacial energies, respectively, and θ is the contact angle measured through the liquid as illustrated in Fig. 20-66. When the solid-vapor interfacial energy exceeds the solid-liquid energy, the fluid wets the solid with a contact angle less than 90°. In the limit of $\gamma^{sv} - \gamma^{sl} \geq \gamma^{lv}$, the contact angle equals 0° and the fluid **spreads** on the solid. The extent of wetting is controlled by the group $\gamma^{lv} \cos \theta$ which is referred to as **adhesion tension.** Sessile drop studies of contact angle can be performed on powder compacts in the same way as on planar surfaces. Methods involve (1) direct measurement of the contact angle from the tangent to the air-binder interface, (2) solution of the Laplace-Young equation involving the contact angle as a boundary condition, or (3) indirect calculations of the contact angle from measurements of e.g., drop height (Ennis & Litster, *The Science & Engineering of Granulation Processes,* Blackie Academic Ltd., 1997). The compact can either be saturated with the fluid for static measurements, or dynamic measurements may be made through a computer-imaging goniometer [Pan et al., *Dynamic Properties of Interfaces & Association Structure,* American Oil Chem. Soc. Press (1995)].

For granulation processes, the dynamics of wetting are often crucial, requiring that powders be compared on the basis of a short time scale, **dynamic contact angle.** Important factors are the physical nature of the powder surface (particle size, pore size, porosity, environment, roughness, pretreatment). Powders which are formulated for granulation often are composed of a combination of ingredients. The dynamic wetting process is therefore influenced by the rates of ingredient dissolution and surfactant adsorption and desorption kinetics. [Pan et al., loc. cit.].

The second approach to characterize wetting considers the ability of the fluid to penetrate a powder bed. It involves the measurement of the extent and rate of fluid rise by capillary suction into a column of powder, better known as the **Washburn test.** Considering the powder to consist of capillaries of radius R, the equilibrium height of rise h_e is determined by equating capillary and gravimetric pressures, or

$$h_e = \frac{2\gamma^{lv} \cos \theta}{\Delta \rho g R} \tag{20-45}$$

where $\Delta\rho$ is the fluid density with respect to air, g is gravity, and $\gamma^{lv} \cos \theta$ is the adhesion tension as before. In addition to the equilibrium height of rise, the dynamics of penetration can be equally important. Ignoring gravity and equating viscous losses with the capillary pressure, the rate (dh/dt) and dynamic height of rise h are given by

$$\frac{dh}{dt} = \frac{R\gamma^{lv} \cos \theta}{4\mu h}, \quad \text{or} \quad h = \sqrt{\left[\frac{R\gamma^{lv} \cos \theta}{2\mu}\right] t} \tag{20-46}$$

where t is time and μ is binder-fluid viscosity. [Parfitt (ed.), *Dispersion of Powders in Liquids,* Elsevier Applied Science Publishers Ltd., 10 (1986).] The grouping of terms in brackets involves the material properties which control the dynamics of fluid penetration, namely average pore radius, or **tortuosity** R (related to particle size and void distribution of the powder), adhesion tension, and binder viscosity.

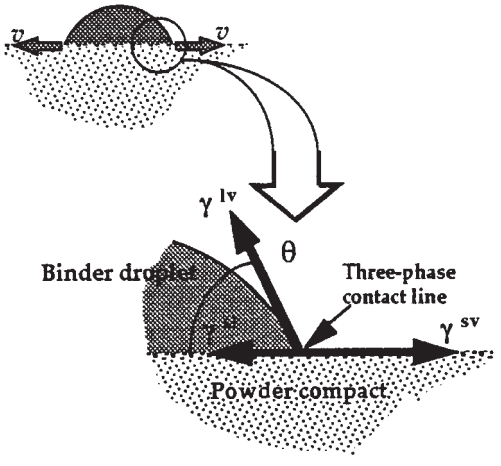


FIG. 20-66 Contact angle on a powder surface, where γ^{sv}, γ^{sl}, γ^{lv} are the solid-vapor, solid-liquid, and liquid-vapor interfacial energies, and θ is the contact angle measured through the liquid.

The contact angle or adhesion tension of a binder solution with respect to a powder can be determined from the slope of the penetration profile. Washburn tests can also be used to investigate the influence of powder preparation on penetration rates. The **Bartell cell** is related to the Washburn test except that adhesion tension is determined by a variable gas pressure which opposes penetration. [Bartell & Osterhof, *Ind. Eng. Chem.,* **19,** 1277 (1927).]

The contact angle of a binder-particle system is not itself a primary thermodynamic quantity, but rather a reflection of individual interfacial energies [Eq. (20-44)] which are a function of the molecular interactions of each phase with respect to one another. An interfacial energy may be broken down into its **dispersion** and **polar** components. These components reflect the chemical character of the interface, with the polar component due to hydrogen bonding and other polar interactions and the dispersion component due to van der Waals interactions. These components may be determined by the wetting tests described here, where a variety of solvents are chosen as the wetting fluids to probe specific molecular interactions as described by Zisman [Contact Angle, Wettability, & Adhesion, *Advances in Chemistry Series,* ACS, **43,** 1 (1964)]. These components of interfacial energy are strongly influenced by trace impurities which often arise in crystallization of the active ingredient, or other forms of processing such as grinding, and they may be modified by judicious selection of **surfactants.** [R. Ayala, Ph.D. Thesis, *Chem. Eng.,* Carnegie Mellon Univ. (1985).] Charges may also exist at interfaces. In the case of solid-fluid interfaces, these may be characterized by **electrokinetic** studies [Shaw, *Introduction to Colloid & Surface Chemistry,* Butterworths & Co. Ltd. (1983)].

The total solid-fluid interfacial energy (i.e., both dispersion and polar components) is also referred to as the **critical solid-surface energy** of the particulate phase. It is equal to the surface tension of a fluid which *just* wets the solid with zero-contact angle. This property of the particle feed may be determined by a third approach to characterize wetting, involving the penetration of particles into a series of fluids of varying surface tension. [R. Ayala, Ph.D. Thesis, *Chem. Eng.,* Carnegie Mellon Univ. (1985).]; Fuerstaneau et al., *Colloids & Surfaces,* **60,** 127 (1991).] The critical surface energy may also be determined from the variation of sediment height with the surface tension of the solvent. [Vargha-Butler, et al., *Colloids & Surfaces,* **24,** 315 (1987).] Distributions in surface energy and its components often exist in practice, and these may be determined by the wetting measurements described here.

Examples of the Impact of Wetting Wetting dynamics has a pronounced influence on the initial nuclei distribution formed from fine powder. The influence of powder-contact angle on the average size of nuclei formed in fluid-bed granulation is illustrated in Fig. 20-67 where contact angle of the powder with respect to water was varied by changing the weight ratios of the ingredients of lactose and salicylic acid, which are hydrophilic and hydrophobic, respectively. [Aulton & Banks, *Proceedings of Powder Technology in Pharmacy Conference,* Powder Advisory Centre, Basel, Switzerland (1979).] Aulton et al. [*J. Pharm. Pharmacol.,* **29,** 59P (1977)] also demonstrated the influence of surfactant concentration on shifting nuclei size due to changes in adhesion tension.

The effect of fluid-penetration rate and the extent of penetration on granule-size distribution for drum granulation was shown by Gluba et al. [*Powder Hand. & Proc.,* **2,** 323 (1990).] Increasing penetration rate increased granule size and decreased asymmetry of the granule-size distribution.

Controlling Wetting Table 20-38 summarizes typical changes in material & operating variables which are necessary to improve wetting uniformity. Also listed are appropriate routes to achieve these changes in a given variable through changes in either the formulation or in processing. Improved wetting uniformity generally implies a tighter granule-size distribution and improved-product quality due to a better-controlled manufacturing process. Eqs. (20-44) to (20-46), shown previously, provide the basic trends of the effect of material variables on both wetting dynamics and wetting extent.

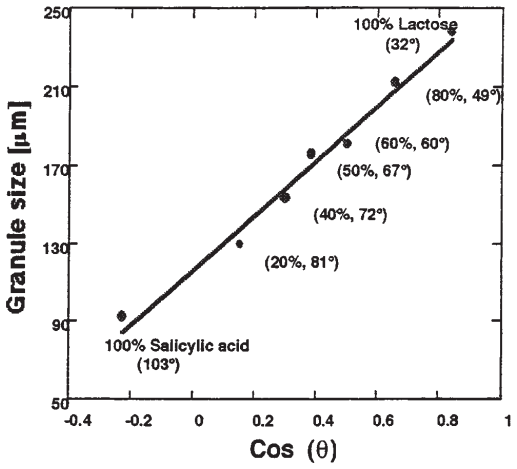


FIG. 20-67 The influence of contact angle on nuclei size formed in fluid-bed granulation of lactose/salicylic acid mixtures. Formulations ranged from hydrophobic (100% salicylic acid) to hydrophilic (100% lactose). Powder contact angle θ was determined by gonimetry and percent lactose of each formulation is given in parentheses. [*Aulton & Banks,* Proceedings of Powder Technology in Pharmacy Conference, *Powder Advisory Centre, Basel, Switzerland (1979).*]

Since drying occurs simultaneously with wetting, the effect of drying can substantially modify the expected impact of a given process variable and this should not be overlooked. In addition, simultaneously drying often implies that the *dynamics* of wetting are far more important than the *extent.*

Adhesion tension should be maximized to increase the rate and extent of both binder spreading and binder penetration. Maximizing adhesion tension is achieved by minimizing contact angle and maximizing surface tension of the binding solution. These two aspects work against one another as surfactant is added to a binding fluid, and in general, there is an optimum surfactant concentration which must be determined for the formulation (R. Ayala, loc. cit.). In addition, surfactant type influences adsorption and desorption kinetics at the three-phase contact line. An inappropriate choice of surfactant can lead to Marangoni interfacial stresses which slow the dynamics of wetting [Pan et al., loc. cit.]. Additional variables which influence adhesion tension include (1) impurity profile and particle habit/morphology typically controlled in the particle-formation stage such as crystallization, (2) temperature of granulation, and (3) technique of grinding, which is an additional source of impurity as well.

Decreases in binder viscosity enhance the rate of both binder spreading and binder penetration. The prime control over the viscosity of the binding solution is through binder concentration. Therefore, liquid loading and drying conditions strongly influence binder viscosity. For processes *without* simultaneous drying, binder viscosity generally decreases with increasing temperature. For processes *with* simultaneous drying, however, the dominantly observed effect is that lowering temperature lowers binder viscosity and enhances wetting due to decreased rates of drying and increased liquid loading.

Changes in particle-size distribution affect the pore distribution of the powder. Large pores between particles enhance the *rate* of binder penetration, whereas they decrease the final *extent.* In addition, the particle-size distribution affects the ability of the particles to pack within the drop as well as the final degree of saturation [Waldie, *Chem. Engin. Sci.,* **46,** 2781 (1991)].

The drop distribution and spray rate of binder fluid have a major influence on wetting. Generally, finer drops will enhance wetting as well as the distribution of binding fluid. The more important question, however, is how large may the drops be or how high of a spray rate is

TABLE 20-38 Controlling Wetting In Granulation Processes*

Typical changes in material or operating variables which improve wetting uniformity	Appropriate routes to alter variable through formulation changes	Appropriate routes to alter variable through process changes
Increase adhesion tension. Maximize surface tension. Minimize contact angle.	Alter surfactant concentration or type to maximize adhesion tension and minimize Marangoni effects. Precoat powder with wettable monolayers, e.g., coatings or steam.	Control impurity levels in particle formation. Alter crystal habit in particle formation. Minimize surface roughness in milling.
Decrease binder viscosity.	Lower binder concentration. Change binder. Decrease any diluents and polymers which act as thickeners.	Raise temperature for processes without simultaneous drying. Lower temperature for processes with simultaneous drying since binder concentration will decrease due to increased liquid loading. This effect generally offsets inverse relationship between viscosity and temperature.
Increase pore size to increase rate of fluid penetration. Decrease pore size to increase extent of fluid penetration.	Modify particle size distribution of feed ingredients.	Alter milling, classification or formation conditions of feed if appropriate to modify particle size distribution.
Improve spray distribution.	Improve atomization by lowering binder fluid viscosity.	Increase wetted area of the bed per unit mass per unit time by increasing the number of spray nozzles, lowering spray rate, increase air pressure or flow rate of two-fluid nozzles.
Increase solids mixing.	Improve powder flowability of feed.	Increase agitation intensity (e.g., impeller speed, fluidization gas velocity, or rotation speed).
Minimize moisture buildup & losses.	Avoid formulations which exhibit adhesive characteristics with respect to process walls.	Maintain spray nozzles to avoid caking and nozzle drip. Avoid spray entrainment in process air streams, and spraying process walls.

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possible. The answer depends on the wetting propensity of the feed. If the liquid loading for a given spray rate exceeds the ability of the fluid to penetrate and spread on the powder, maldistribution in binding fluid will develop in the bed. This maldistribution increases with increasing spray rate, increasing drop size, and decreasing spray area (due to, e.g., bringing the nozzle closer to the bed or switching to fewer nozzles). The maldistribution will lead to large granules on the one hand and fine ungranulated powder on the other. In general, the width of the granule-size distribution will increase and generally the average size will decrease. Improved spray distribution can be aided by increases in agitation intensity (e.g., mixer impeller or chopper speed, drum rotation rate, or fluidization gas velocity) and by minimizing moisture losses due to spray entrainment, dripping nozzles, or powder caking on process walls.

GROWTH AND CONSOLIDATION

The evolution of the granule-size distribution of a particulate feed in a granulation process is controlled by several mechanisms, as illustrated in Table 20-39. These include the **nucleation** of fine powder to form initial primary granules, the **coalescence** of existing granules and the **layering** of raw material onto previously formed nuclei or granules. Granules may simultaneously be compacted by **consolidation** and reduced in size by **breakage.** There are strong interactions between these rate processes. Dominant mechanisms of growth and consolidation are dictated by the relationship between critical particle properties and operating variables as well as by mixing, size distribution, and the choice of processing.

Growth Physics and Contact Mechanics In order for two colliding granules to coalesce rather than break up, the **collisional kinetic energy** must first be dissipated to prevent rebound as illustrated in Fig. 20-68. In addition, the strength of the bond must resist any subsequent breakup forces due to **bed agitation intensity.** The ability of the granules to **deform** during processing increases the bonding or **contact area** thereby dissipating breakup forces and has a large effect on growth rate. From a balance of binding and separating forces and torque acting within the area of granule contact, Ouchiyama & Tanaka [*I & EC Proc. Des. & Dev.*, **21,** 29 (1982)] derived a **critical limit of size** above which coalescence becomes impossible, given by

TABLE 20-39 Growth and Breakage Mechanisms in Granulation Processes

Granule growth	Granule breakage
Nucleation $jp_1 \rightarrow P_j$	Shatter $P_j \rightarrow jp_1$
Coalescence $P_i + P_j \rightarrow P_{i+j}$	Fragmentation $P_j \rightarrow P_j + P_{i-j}$
Layering $P_i + jp_1 \rightarrow P_{i+j}$	Wear $P_i \rightarrow P_{i-j} + jp_1$
Abrasion transfer $P_i + P_j \rightarrow P_{i+1} + P_{j-1}$ or $P_{i-1} + P_{j+1}$	
Free fines P_1	Working unit P_i

*After Sastry and Fuerstenau in *Agglomeration '77*, Sastry (ed.), *AIME*, New York, 381 (1977).

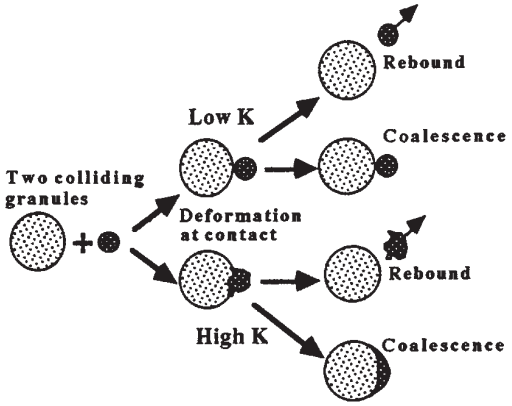


FIG. 20-68 Mechanisms of granule coalescence for low- and high-deformability systems. Rebound occurs for average granule sizes greater than the critical granule size D_c. K = deformability.

$$D_c = (AQ^{3\zeta/2}K^{3/2}\sigma_T)^{1/[4-(3/2)\eta]} \qquad (20\text{-}47)$$

K is **deformability,** a proportionality constant relating the maximum compressive force Q to the deformed-contact area, A is a constant with units of (L^3/F) which relates granule volume to impact compression force and σ_T is the **tensile strength** of the granule bond [see Eq. (20-43)]. The parameters ζ and η depend on the deformation mechanism acting within the contact area, with their values bounded by the cases of complete plastic or complete elastic deformation. For plastic deformation, $\zeta = 1$, $\eta = 0$, and $K \propto 1/H$ where H is hardness. For elastic, Hertzian deformation, $\zeta = \frac{2}{3}$, $\eta = \frac{2}{3}$, and $K \propto (1/E^*)^{2/3}$ where E^* is reduced elastic modulus. Granule deformation is generally dominated by **inelastic** behavior of the contacts during collision, with such deformation treated by the area of inelastic **contact mechanics.** [Johnson, *Contact Mechanics*, Cambridge University Press (1985).]

The value D_c represents a harmonic **average** granule size. Therefore, it is possible for the collision of two large granules to be unsuccessful, their average being beyond this critical size, whereas the collision of a large and small granule leads to successful coalescence. D_c is a strong function of moisture, as illustrated in Fig. 20-69 by the marked increase in average granule size with moisture which is related to deformability.

Granules are compacted as they collide due to bed agitation intensity. This process of **granule consolidation** expels pore fluid to the granule surface, thereby increasing local liquid saturation in the contact area of colliding granules. This surface fluid (1) increases the tensile strength of the liquid bond σ_T, and (2) increases surface plasticity and deformability K. Equation (20-47) shows that these factors generally increase the extent of granule growth, particularly for systems of low deformability. In such **low-deformability systems,** growth is largely controlled by the extent of this fluid layer. For **deformable systems,** however, the combined effect of these increases is more complex. Deformability K is related to both the **yield strength** of the material σ_y, i.e., the ability of the material to resist stresses, and the ability of the surface to be strained without degradation or rupture of the granule, with this maximum allowable **critical deformation strain** denoted by $(\Delta L/L)_c$. Figure 20-70 illustrates the stress-strain behavior of cylindrical compact agglomerates during compression as a function of liquid saturation, with **strain** denoted by $\Delta L/L$. In general, high deformability K requires low yield strength σ_y and high critical strain $(\Delta L/L)_c$. For this formulation, increasing moisture increases deformability by lowering interparticle frictional resistance which also increases mean granule size (Fig. 20-69).

Effect of Equipment Mechanical Variables The importance of deformability to the growth process depends on **bed agitation intensity** in comparison to the strength of the formed granules for agitative granulation processes. **Low agitation intensity** processes include fluid-bed, drum, and pan granulators. **High agitation intensity** processes include pin and plow shear-type mixers, and high-shear

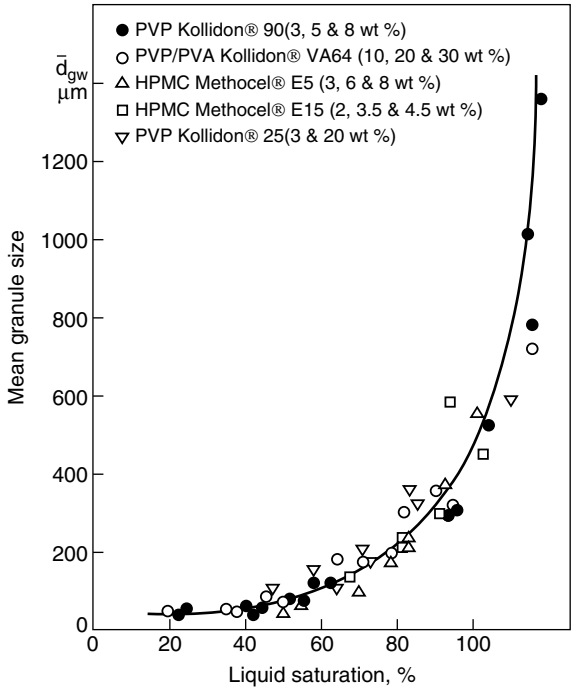


FIG. 20-69 Effect of moisture as a percentage of granule saturation on mean granule diameter, indicating the marked increase in granule deformability with increased moisture. Mean granule diameter is a measure of the critical limit of size D_c. Granulation of calcium hydrogen phosphate with aqueous binder solutions in a Fielder PMAT 25 VG high-shear mixer. [*Ritala et al.,* Drug Dev. & Ind. Pharm., ***14****(8), 1041 (1988).*]

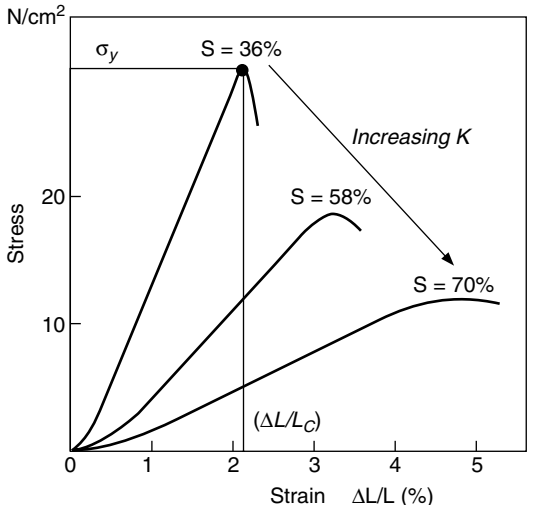


FIG. 20-70 The influence of moisture as a percentage of sample saturation S on granule deformability. Here, deformation strain $(\Delta L/L)$ is measured as a function of applied stress, with the peak stress and strain denoted by tensile strength σ_y and critical strain $(\Delta L/L)_c$ of the material. Dicalcium phosphate with a 15 wt % binding solution of PVP/PVA Kollidon® VA64. [*Holm et al.,* Powder Tech., ***43,*** *213 (1985).*] With kind permission from Elsevier Science SA, Lausanne, Switzerland.

mixers involving choppers. Bed agitation intensity and compaction pressure are controlled by **mechanical variables** of the process such as fluid-bed excess gas velocity or mixer-impeller speed. Agitation intensity controls the relative **collisional velocities** of granules within the process and therefore growth, breakage, consolidation, and final-product density. Figure 20-71 summarizes typical characteristic velocities, agitation intensities and compaction pressures, and product-relative densities achieved for a variety of size-enlargement processes.

Low-Agitation Intensity Growth For low-agitation processes, consolidation of the granules occurs at a much slower rate than growth, and granule deformation can be ignored to a first approximation. The growth process can be modeled by the collision of two rigid granules each coated by a liquid layer of thickness h. The probability of successful coalescence is governed by a dimensionless **Stokes number *St*** given by

$$St = \frac{4\rho u_0 d}{9\mu} \tag{20-48}$$

where u_0 is the relative collisional velocity of the granules, ρ is granule density, d is the harmonic average of granule diameter, and μ is the solution phase binder viscosity. The Stokes number represents the ratio of initial collisional kinetic energy to the energy dissipated by viscous lubrication forces, and it is one measure of normalized bed agitation energy. (The granule Stokes number is akin to the particle Reynolds number in two-phase systems.) Successful growth by coalescence or layering requires that

$$St < St^* \quad \text{where} \quad St^* = \left(1 + \frac{1}{e_r}\right) \ln (h/h_a) \tag{20-49}$$

where St^* is a critical Stokes number representing the energy required for rebound. The binder layer thickness h is related to liquid loading, e_r is the coefficient of restitution of the granules and h_a is a measure of surface roughness or asperities. The critical condition given by Eq. (20-49) controls the growth of low-deformability systems (Fig. 20-68). [Ennis et al., *Powder Tech.,* **65,** 257 (1991).]

Both the **binder solution viscosity** μ and the granule density are largely properties of the feed. Binder viscosity is also a function of local temperature, collisional strain rate (for non-Newtonian binders) and binder concentration. It can be controlled as discussed above through judicious selection of binding and surfactant agents and measured by standard rheological techniques. [Bird et al., *Dynamics of Polymeric Liquids,* vol. 1, John Wiley & Sons, Inc. (1977)]. The **collisional velocity** is a function of process design and operating variables, and is related to bed agitation intensity and mixing. Possible choices of u_0 are summarized in Fig. 20-71. Note that u_0 is an interparticle collisional velocity, which is not necessarily the local average granular flow velocity.

Three regimes of granule growth may be identified for low-agitation intensity processes [Ennis et al., *Powder Tech.,* **65,** 257 (1991)]. For small granules or high binder viscosity lying within a **noninertial regime** of granulation, all values of *St* will lie below the critical value St^* and therefore all granule collisions result in successful growth *provided* binder is present. Growth rate is independent of granule kinetic energy, particle size, and binder viscosity (provided other rate processes are constant). Distribution of binding fluid then controls growth, and this is strongly coupled with the rate process of wetting. (See subsection "Wetting.") As granules grow in size, their collisional momentum increases, leading to localized regions in the process where *St* exceeds the critical value St^*. In this **inertial regime** of granulation, granule size, binder viscosity, and collision velocity determine the proportion of the bed in which granule rebound is possible. Increases in binder viscosity and decreases in agitation intensity increase the extent of granule growth. When the spatial average of *St* exceeds St^*, growth is balanced by granule disruption or breakup, leading to the **coating regime** of granulation. Growth continues by coating of granules by binding fluid alone. Transitions between granulation regimes depends on bed hydrodynamics. As demonstrated by Ennis et al. [*Powder Tech.,* **65,** 257 (1991)], granulation of an initially fine powder may exhibit characteristics of all three granulation regimes as time progresses, since *St* increases with increasing granule size. Implications and additional examples regarding the regime analysis are highlighted by Ennis [*Powder Tech.,* **88,** 203 (1996).]

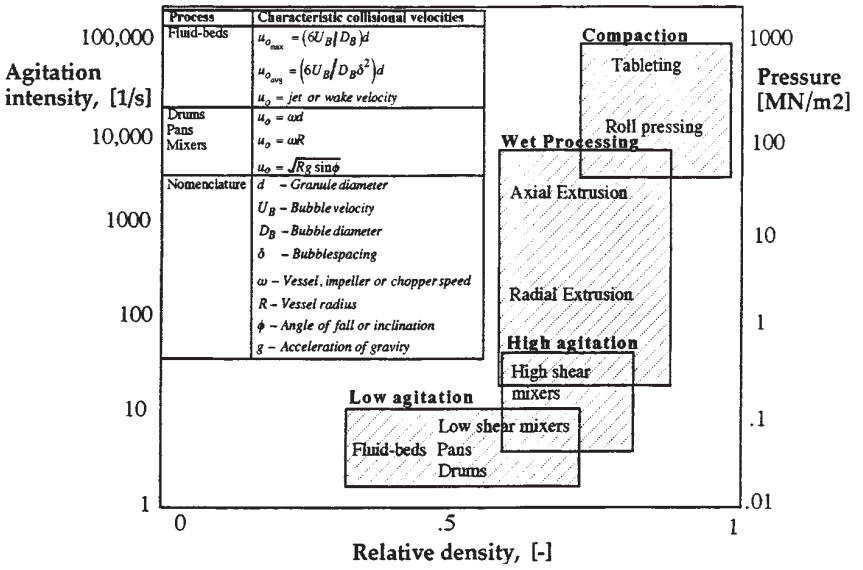


FIG. 20-71 Classification of agglomeration processes by agitation intensity and compaction pressure. Relative density is with respect to primary particle density and equals $(1 - \varepsilon)$ where ε is the solid volume fraction. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries,* Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

High-Agitation Intensity Growth For **high-agitation** processes involving **high-shear mixing** granule deformability and plastic deformation can no longer be neglected as they occur at the same rate as granule growth. Typical growth profiles for high-shear mixers are illustrated in Fig. 20-72. Two stages of growth are evident, which reveal the possible effects of binder viscosity and impeller speed. The *initial, non-equilibrium stage of growth* is controlled by granule deformability, and is of most practical significance in manufacturing. Increases in *St* due to lower viscosity or higher impeller speed increase the rate of growth as shown in Fig. 20-72, since the system becomes more deformable and easier to **knead** into larger-granule structures. These effects are contrary to what is predicted from the Stokes analysis based on rigid, elastic granules.

Growth continues until disruptive and growth forces are balanced in the process. This last *equilibrium stage of growth* represents a balance between dissipation and collisional kinetic energy, and so increases in *St* decrease the final granule size, as expected from the Stokes analysis. Note that the equilibrium-granule diameter decreases with the inverse square root of the impeller speed, as it should based on $St = St^*$ with $u_0 = d \cdot (du/dx) = \omega d$. The Stokes analysis is used to determine the effect of operating variables and binder viscosity on *equilibrium* growth, where disruptive and growth forces are balanced.

In the early stages of growth for high-shear mixers, the Stokes analysis in its present form is inapplicable. Freshly formed, uncompacted granules are easily deformed, and as growth proceeds and consolidation of granules occur, they will surface harden and become more resistant to deformation. This increases the importance of the elasticity of the granule assembly. Therefore, in later stages of growth, older granules approach the ideal Stokes model of rigid, elastic collisions. For these reasons, the Stokes approach has had reasonable success in providing an overall framework with which to compare a wide variety of granulating materials [Ennis, *Powder Tech.,* **88,** 203 (1996)]. In addition, the Stokes number controls in part the degree of deformation occurring during a collision since it represents the importance of collision kinetic energy in relation to viscous dissipation, although the exact dependence of deformation on *St* is presently unknown.

Extent of Noninertial Growth Growth by coalescence in granulation processes may be modeled by the population balance. (See the Modeling and Simulation subsection.) It is necessary to determine both the mechanism and kernels which describe growth. For fine powders within the noninertial regime of growth, all collisions result in successful coalescence *provided* binder is present. Coalescence occurs via a random, size-independent kernel which is only a function of liquid loading *y,* or

$$\beta(u,v) = k = k^* f(y) \tag{20-50}$$

The dependence of growth on liquid loading $f(y)$ strongly depends on wetting properties. For random growth, it may be shown that the average granule size increases exponentially with time, or $d = d_0 e^{kt}$, and that the **maximum extent** of granulation $(kt)_{\max}$ occurring within the noninertial regime is given by

$$(kt)_{\max} = 6 \ln \left(\frac{St^*}{St_0} \right) \tag{20-51}$$

$$(kt)_{\max} \propto \ln \left(\frac{\mu}{\rho u_0 d_0} \right) \tag{20-52}$$

St_0 is the Stokes number based on initial nuclei diameter d_0 [Adetayo et al., *Powder Tech.,* **82,** 37 (1995)]. Extent $(kt)_{max}$ depends logarithmically on binder viscosity and inversely on agitation velocity. Maximum granule size depends linearly on these variables. Also, $(kt)_{max}$ has been observed to depend linearly on liquid loading *y.* Therefore, the maximum granule size depends exponentially on liquid loading. Fig. 20-73 illustrates this normalization of extent $(kt)_{max}$ for the drum granulation of limestone and fertilizers.

Determination of *St** The extent of growth is controlled by some limit of granule size, either reflected by the critical Stokes number St^* or by the critical limit of granule size D_c. There are three possible methods to determine this critical limit. The first involves measuring the critical rotation speed for the survival of a series of liquid-binder drops during drum granulation [Ennis, Ph.D. Thesis (1990)]. A second refined version involves measuring the survival of granules in a couette-fluidized shear device [Tardos & Khan, AIChE Annual Meeting, Miami (1995)]. Both the onset of granule deformation and complete granule rupture are determined from the dependence of granule shape and the number of surviving granules,

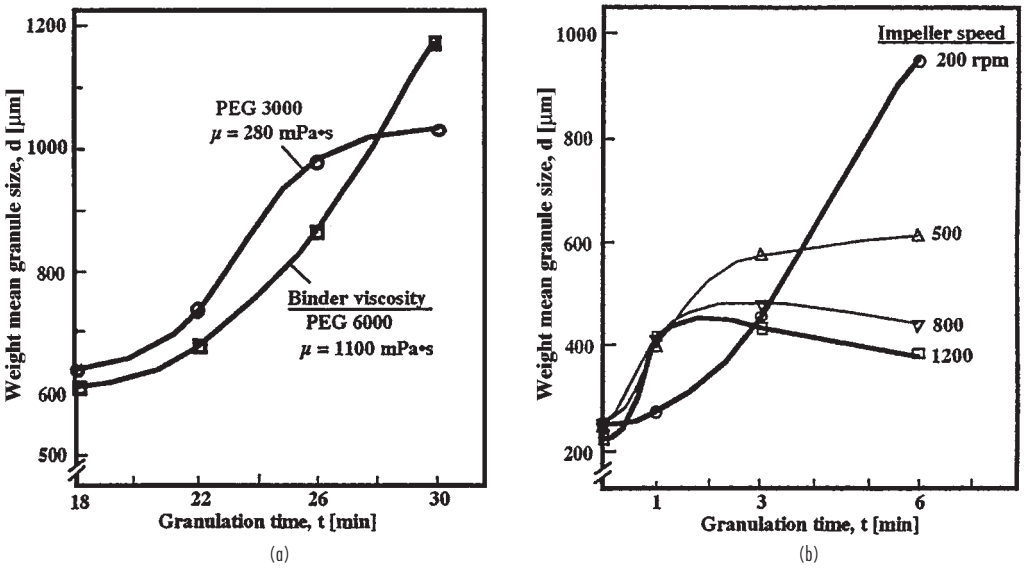


FIG. 20-72 Granule diameter as a function of time for high-shear mixer granulation, illustrating the influence of deformability on growth behavior. (*a*) 10-liter vertical high-shear melt granulation of lactose with liquid loading of 15 wt % binder and impeller speed of 1400 rpm for two different viscosity grades of polyethylene glycol binders. [*Schaefer et al.,* Drug Dev. & Ind. Pharm., ***16****(8), 1249 (1990)*]. (*b*) 10-liter vertical high-shear mixer granulation of dicalcium phosphate with 15 wt % binder solution of PVP/PVA Kollidon® VA64, liquid loading of 16.8 wt % and chopper speed of 1000 rpm for varying impeller speed. [*Schaefer et al.,* Pharm. Ind., ***52****(9), 1147 (1990).*]

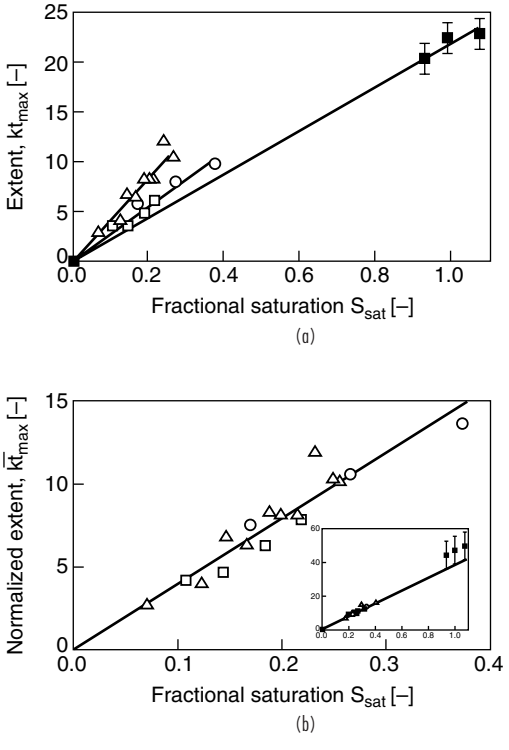


FIG. 20-73 (*a*) Maximum extent of noninertial growth $(kt)_{max}$ as a function of fractional saturation of the powder feed S_{sat} for drum granulation, and (*b*) maximum extent normalized for differences in St_0. Feed powders: ammonium sulfate (○); monoammonium phosphate (□), diammonium phosphate (△), limestone (■). [*Adetayo et al.,* Powder Tech., ***82,*** *37 (1995).*] With kind permission from Elsevier Science SA, Lausanne, Switzerland.

respectively, on shear rate. Granule breakdown and deformation are controlled by a generalization of *St,* or a yield number *Y* given by

$$Y = \frac{\rho u_0^2}{\tau_y} = \frac{\rho (du_0/dx)^2 d^2}{\tau_y} \tag{20-53}$$

Viscosity has been replaced by a generalized form of plastic deformation controlled by a yield stress τ_y, which may be determined by compression experiments. Compare with Eq. (20-48). The critical shear rate describing complete granule rupture defines St^*, whereas the onset of deformation and the beginning of granule breakdown defines an additional critical value St^y.

The last approach is to measure the deviation in the growth-rate curve from random exponential growth [Adetayo & Ennis, *AIChE J.,* (1997)]. The deviation from random growth indicates a value of w^*, or the **critical granule diameter** at which noninertial growth ends. This value is related to D_c. (See the Modeling and Simulation subsection for further discussion.)

Consolidation Consolidation of granules determines **granule porosity,** and hence **granule density.** Granules may consolidate over extended times and achieve high densities if there is no simultaneous drying to stop the consolidation process. The extent and rate of consolidation are determined by the balance between the collision energy and the granule resistance to deformation. Decreasing feed-particle size decreases the rate of consolidation due to the high specific surface area and low permeability of fine powders. The effects of binder viscosity and liquid content are complex and interrelated. For low-viscosity binders, consolidation *increases* with liquid content, but for high-viscosity binders consolidation *decreases* with increasing liquid content (see Fig. 20-74). The exact effect of liquid content and binder viscosity is determined by the balance between viscous dissipation and particle frictional losses and is difficult to predict [Iveson et al., *Powder Tech.,* (1996)]. Increasing agitation intensity increases the degree of consolidation by increasing the energy of collision and compaction.

Controlling Growth and Consolidation Table 20-40 summarizes typical changes in material & operating variables which maximize granule growth and consolidation. Also listed are appropriate routes to achieve these changes in a given variable through changes in either the formulation or in processing. Growth and consolidation of

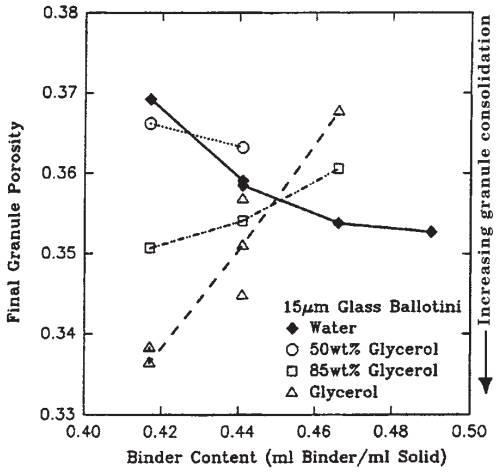


FIG. 20-74 Effect of binder viscosity and liquid content on final granule porosity for the drum granulation of 15 μm glass ballotini. Decreasing granule porosity corresponds to increasing extent of granule consolidation. [*Iveson et al.,* Powder Tech., **88,** 15 *(1996).*] With kind permission from Elsevier Science SA, Lausanne, Switzerland.

granules are strongly influenced by *St.* Increasing *St* increases energy with respect to dissipation during deformation of granules. Therefore, the rate of growth for deformable systems (e.g., deformable formulation or high-shear mixing) and the rate of consolidation of granules generally increases with increasing *St. St* may be increased by decreasing binder viscosity or increasing agitation intensity. Changes in binder viscosity may be accomplished by formulation changes (e.g., the type or concentration of binder) or by operating temperature changes. In addition, simultaneous drying strongly influences the effective binder concentration and viscosity. The *maximum* extent of growth increases with decreasing *St* and increased liquid loading, as reflected by Eqs. (20-50) and (20-51). Increasing particle size also increases the rate of consolidation, and this can be modified by upstream milling or crystallization conditions.

BREAKAGE

A granule is a nonuniform **physical composite** possessing certain macroscopic mechanical properties, such as a generally anisotropic yield stress, as well as an inherent flaw distribution. Hard materials may fail in tension (see brittle fracture under size reduction), with the breaking strength being much less than the inherent tensile strength of bonds because of the existence of flaws. [Lawn, *Fracture of Brittle Solids,* 2d ed., Cambridge University Press (1975).] Bulk breakage tests of granule strength measure both the inherent bond strength of granule as well as its flaw distribution. [Bemros & Bridgwater, *Powder Tech.,* **49,** 97 (1987).] In addition, the mechanism of granule breakage (Table 20-39) is a strong function of materials properties of the granule itself as well as the type of loading imposed by the test conditions. Ranking of product-breakage resistance by ad hoc tests may be test specific, and in the worst case differ from actual process conditions. Standardarized mechanical tests should be employed instead to measure material properties which *minimize* the effect of flaws and loading conditions under well-defined geometries of internal stress, as described below.

Fracture Properties **Fracture toughness** defines the stress distribution in the body just before fracture and is given by

$$K_c = Y\sigma_f\sqrt{\pi c} \tag{20-54}$$

TABLE 20-40 Controlling Growth and Consolidation in Granulation Processes*

Typical changes in material or operating variables which maximize growth and consolidation	Appropriate routes to alter variable through formulation changes	Appropriate routes to alter variable through process changes
Rate of growth (low deformability):		
Increase rate of nuclei formation	Improve wetting properties. (See "Wetting" subsection.) Increase binder distribution.	Increase spray rate and number of drops.
Increase collision frequency		Increase mixer impeller or drum rotation speed or fluid-bed gas velocity.
Increase residence time		Increase batch time or lower feed rate.
Rate of growth (high deformability):		
Decrease binder viscosity	Decrease binder concentration or change binder. Decrease any diluents and polymers which act as thickeners.	Decrease operating temperature for systems with simultaneous drying. Otherwise increase temperature.
Increase agitation intensity		Increase mixer impeller or drum rotation speed or fluid-bed gas velocity.
Increase particle density		
Increase rate of nuclei formation, collision frequency & residence time, as above for low deformability systems.		
Extent of growth:		
Increase binder viscosity	Increase binder concentration, change binder, or add diluents and polymers as thickeners.	Increase operating temperature for systems with simultaneous drying. Otherwise decrease temperature.
Decrease agitation intensity		Decrease mixer impeller or drum rotation speed or fluid-bed gas velocity.
Decrease particle density		
Increase liquid loading		Extent observed to increase linearly with moisture.
Rate of consolidation:		
Decrease binder viscosity	As above for high deformability systems.	As above for high deformability systems. In addition, increase compaction forces by increasing bed weight, or altering mixer impeller or fluid-bed distributor plate design.
Increase agitation intensity	Particle size and friction strongly interact with binder viscosity to control consolidation. Feed particle size may be increased and fine tail of distribution removed.	
Increase particle density		
Increase particle size		Size is controlled in milling and particle formation.

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where σ_f is the applied fracture stress, c is the length of the crack in the body, and Y is a calibration factor introduced to account for different body geometries. (Lawn, loc. cit.)

The elastic stress cannot exceed the **yield stress** of the material, implying a region of local yielding at the crack tip. Nevertheless, to apply the simple framework of linear elastic fracture mechanics, Irwin [*J. Applied Mechanics,* **24,** 361 (1957)] proposed that this **process zone size** r_p be treated as an *effective* increase in crack length δc. Fracture toughness is then given by

$$K_c = Y\sigma_f\sqrt{\pi(c+\delta c)} \quad \text{with} \quad \delta c \sim r_p \tag{20-55}$$

The process zone is a measure of the yield stress or plasticity of the material in comparison to its brittleness. Yielding within the process zone may take place either plastically or by diffuse microcracking, depending on the brittleness of the material. For plastic yielding, r_p is also referred to as the **plastic zone size.**

The **critical strain energy release rate** G_c is the energy equivalent to fracture toughness, first proposed by Griffith [*Phil. Trans. Royal Soc.,* **A221,** 163 (1920)]. They are related by

$$G_c = K_c^2/E \tag{20-56}$$

Fracture Measurements In order to ascertain fracture properties in any reproducible fashion, very specific test geometry must be used since it is necessary to know the stress distribution at predefined, induced cracks of known length. Three traditional methods are (1) the **three-point bend test,** (2) **indentation fracture testing,** and (3) **Hertzian contact compression** between two spheres of the material (See fracture under size reduction). In the case of the three-point bend test, toughness is determined from the variance of fracture stress on induced crack length, as given by Eq. (20-55) where δc is initially taken as zero and determined in addition to toughness. (Ennis & Sunshine, *Tribology International,* **26,** 319 (1993).) In the case of indentation fracture, one determines **hardness** H from the area of the residual plastic impression and fracture toughness from the lengths of cracks propagating from the indent as a function of indentation load F. [Johnsson & Ennis, *Proceedings of the First International Particle Technology Forum,* vol. 2, AIChE, Denver, 178 (1994).] Hardness is a measure of the yield strength of the material. Toughness and hardness in the case of indentation are given by

$$K_c = \beta\sqrt{\frac{E}{H}}\frac{F}{c^{3/2}} \quad \text{and} \quad H \sim \frac{F}{A} \tag{20-57}$$

Table 20-41 compares typical fracture properties of agglomerated materials. Fracture toughness K_c is seen to range from 0.01 to 0.06 MPa·m$^{1/2}$, less than that typical for polymers and ceramics, presumably due to the high agglomerate voidage. Critical strain energy release rates G_c from 1 to 200 J/m^2, typical for ceramics but less than that for polymers. Process zone sizes δc are seen to be large and of the order of 0.1–1 mm, values typical for polymers. Ceramics on the other hand typically have process zone sizes less than 1 μm. Critical displacements required for fracture may be estimated by the ratio G_c/E, which is an indication of the **brittleness** of the material. This value was of the order of 10^{-7}–10^{-8} mm for polymer-glass agglomerates, similar to polymers, and of the order of 10^{-9} mm for herbicide bars, similar to ceramics. In summary, granulated materials behave similar to brittle ceramics which have small critical displacements and yield strains but also similar to ductile polymers which have large process or plastic zone sizes.

Mechanisms of Breakage The process zone plays a large role in determining the mechanism of granule breakage (Table 20-39). [Ennis & Sunshine, loc. cit.] Agglomerates with process zones small in comparison to granule-size break by a brittle-fracture mechanism into smaller fragments, or **fragmentation** or **fracture.** On the other hand for agglomerates with process zones of the order of their size, there is insufficient volume of agglomerate to concentrate enough elastic energy to propagate gross fracture during a collision. The mechanism of breakage for these materials is one of **wear, erosion,** or **attrition** brought about by diffuse microcracking. In the limit of very weak bonds, agglomerates may also **shatter** into small fragments or primary particles.

Each mechanism of breakage implies a different functional dependence of breakage rate on material properties. For the case of **abrasive wear** of ceramics due to surface scratching by loaded indentors, Evans & Wilshaw [*Acta Metallurgica,* **24,** 939 (1976)] determined a volumetric wear rate V of

$$V = \frac{d_i^{1/2}}{A^{1/4}K_c^{3/4}H^{1/2}}P^{5/4}l \tag{20-58}$$

where d_i is indentor diameter, P is applied load, l is wear displacement of the indentor and A is apparent area of contact of the indentor with the surface. Therefore, wear rate depends inversely on fracture toughness. For the case of fragmentation, Yuregir et al. [*Chem. Eng. Sci.,* **42,** 843 (1987)] have shown that the fragmentation rate of organic and inorganic crystals is given by

$$V \sim \frac{H}{K_c^2}\rho u^2 a \tag{20-59}$$

where a is crystal length, ρ is crystal density, and u is impact velocity. Note that hardness plays an opposite role for fragmentation than for wear, since it acts to concentrate stress for fracture. Fragmentation rate is a stronger function of toughness as well.

Drawing on analogies with this work, the breakage rates by wear B_w and fragmentation B_f for fluid-bed processing should be of the forms:

$$B_w = \frac{d_0^{1/2}}{K_c^{3/4}H^{1/2}}h_b^{5/4}(U-U_{mf}) \tag{20-60}$$

$$B_f \sim \frac{H}{K_c^2}\rho(U-U_{mf})^2 a \tag{20-61}$$

where d is granule diameter, d_0 is primary particle diameter, $(U - U_{mf})$ is fluid-bed excess gas velocity, and h_b is bed height. Fig. 20-75 illustrates the dependence of erosion rate on material properties for granules undergoing a wear mechanism of breakage, as governed by Eq. (20-60).

Controlling Breakage Table 20-42 summarizes typical changes in material & operating variables which are necessary to minimize breakage. Also listed are appropriate routes to achieve these changes in a given variable through changes in either the formulation or in processing. Both fracture toughness and hardness are strongly influenced by the compatibility of the binder with the primary particles, as well as the elastic/plastic properties of the binder. In addition, hardness and toughness increase with decreasing voidage and are influenced by

TABLE 20-41 Fracture Properties of Agglomerated Materials*

Material	K_c (MPa.m$^{1/2}$)	G_c (J/m^2)	δc (μm)	E (MPa)	G_c/E (m)
Bladex 60™†	0.070	3.0	340	567	5.29e–09
Bladex 90™†	0.014	0.96	82.7	191	5.00e–09
Glean™†	0.035	2.9	787	261	1.10e–08
Glean Aged™†	0.045	3.2	3510	465	6.98e–09
CMC-Na (M)‡	0.157	117.0	641	266	4.39e–07
Klucel GF‡	0.106	59.6	703	441	1.35e–07
PVP 360K‡	0.585	199.0	1450	1201	1.66e–07
CMC 2% 1kN‡	0.097	16.8	1360	410	4.10e–08
CMC 2% 5kN‡	0.087	21.1	1260	399	5.28e–08
CMC 5% 1kN‡	0.068	15.9	231	317	5.02e–08

*Ennis & Sunshine, *Tribology International,* **26,** 319 (1993)
†DuPont corn herbicides
‡50 μm glass beads with polymer binder

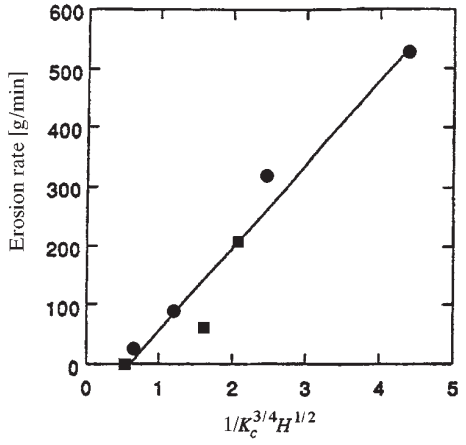


FIG. 20-75 Fluid-bed erosion or wear rate as a function of granule material properties. K_C is fracture toughness and H is hardness as measured by three-point bend tests. [*Ennis & Sunshine,* Tribology International, ***26,*** *319 (1993).*]

previous consolidation of the granules (see subsection of Growth and Consolidation). While the direct effect of increasing gas velocity and bed height is to increase breakage of dried granules, increases in these variables may also act to increase consolidation of wet granules, lower voidage, and therefore lower the final-breakage rate. Granule structure also influences breakage rate, e.g., a layered structure is less prone to breakage than a raspberry-shaped agglomerate. However, it may be impossible to compensate for extremely low toughness by changes in structure. Measurements of fracture properties help define expected breakage rates for a product and aid product development of formulations.

POWDER MECHANICS & POWDER COMPACTION

The ability of powders to freely flow, easily compact, and maintain strength during stress unloading determines the success of compaction techniques of agglomeration. These attributes are strongly influenced by mechanical properties of the feed. [Brown & Richards, *Principles of Powder Mechanics,* Pergamon Press (1970).] The flow properties summarized below are also relevant to the design of bulk powder handling systems such as feeders and hoppers [see Section 21 & Carson & Marinelli, *Chemical Eng.,* April (1994)].

Powder Mechanics Measurements As opposed to fluids, powders may withstand applied shear stress similar to a bulk solid due to **interparticle friction.** As the applied shear stress is increased, the powder will reach a maximum sustainable shear stress τ, at which point it yields or flows. This limit of shear stress τ increases with increasing applied normal load σ, with the functional relationship being referred to as a **yield locus.** A well-known example is the Mohr-Coulomb yield locus, or

$$\tau = c + \mu\sigma = c + \sigma \tan \phi \qquad (20\text{-}62)$$

Here, μ is the coefficient of internal friction, ϕ is the internal angle of friction, and c is the shear strength of the powder in the absence of any applied normal load. The yield locus of a powder may be determined from a **shear cell,** which typically consists of a cell composed of an upper and lower ring. The normal load is applied to the powder vertically while shear stresses are measured while the lower half of the cell is either translated or rotated [Carson & Marinelli, loc. cit.]. Over-

TABLE 20-42 Controlling Breakage in Granulation Processes*

Typical changes in material or operating variables which minimize breakage	Appropriate routes to alter variable through formulation changes	Appropriate routes to alter variable through process changes
Increase fracture toughness Maximize overall bond strength Minimize agglomerate voidage	Increase binder concentration or change binder. Bond strength strongly influenced by formulation and compatibility of binder with primary particles.	Decrease binder viscosity to increase agglomerate consolidation by altering process temperatures (usually decrease for systems with simultaneous drying). Increase bed-agitation intensity (e.g., increase impeller speed, increase bed height) to increase agglomerate consolidation. Increase granulation-residence time to increase agglomerate consolidation, but minimize drying time.
Increase hardness to reduce wear Minimize binder plasticity Minimize agglomerate voidage	Increase binder concentration or change binder. Binder plasticity strongly influenced by binder type.	See above effects which decrease agglomerate voidage.
Decrease hardness to reduce fragmentation Maximize binder plasticity Maximize agglomerate voidage	Change binder. Binder plasticity strongly influenced by binder type. Apply coating to alter surface hardness.	Reverse the above effects to increase agglomerate voidage.
Decrease load to reduce wear	Lower-formulation density.	Decrease bed-agitation and compaction forces (e.g., mixer impeller speed, fluid-bed height, bed weight, fluid-bed excess gas velocity, drum rotation speed).
Decrease contact displacement to reduce wear		Decrease contacting by lowering mixing and collision frequency (e.g., mixer impeller speed, fluid-bed excess gas velocity, drum rotation speed).
Decrease impact velocity to reduce fragmentation	Lower-formulation density.	Decrease bed-agitation intensity (e.g., mixer impeller speed, fluid-bed excess gas velocity, drum rotation speed). Also strongly influenced by distributor-plate design in fluid-beds, or impeller and chopper design in mixers.

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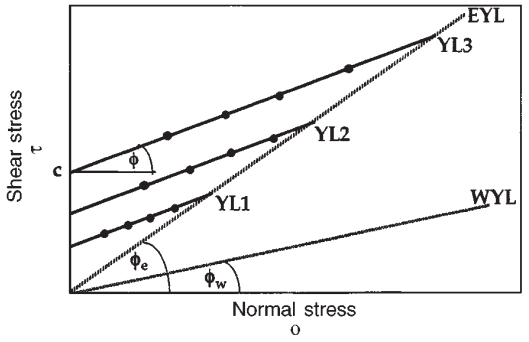


FIG. 20-76 The yield loci of a powder, reflecting the increased shear stress required for flow as a function of applied normal load. YL1 through YL3 represent yield loci for increasing previous compaction stress. EYL and WYL are the effective and wall yield loci, respectively.

compacted powders dilate when sheared, and the ability of powders to change volume with shear results in the powder's shear strength τ being a strong function of previous compaction. There are therefore a series of *yield loci* (YL) as illustrated in Fig. 20-76 for increasing previous **compaction stress.** The individual yield loci terminate at a critical state of stress, which when joined together form the *effective yield locus* (EYL) which typically passes through the stress-strain origin, or

$$\tau = \mu_e \sigma = \sigma \tan \phi_e \qquad (20\text{-}63)$$

This line represents the critical shear stress that a powder can withstand which has not been over or underconsolidated, i.e., the stress typically experienced by a powder which is in a constant state of shear. When sheared powders also experience friction along a wall, this relationship is described by the wall yield locus, or

$$\tau = \mu_w \sigma = \sigma \tan \phi_w \qquad (20\text{-}64)$$

The angles ϕ_e and ϕ_w are the **effective angle** and **wall angle of friction,** respectively.

A powder's strength increases significantly with increasing previous compaction. The relationship between the unconfined yield stress f_c, or a powder's strength, and compaction pressure σ_c is described by the powder's **flow function** *FF.* The flow function is the paramount characterization of powder strength and flow properties, and it is calculated from the yield loci determined from shear cell measurements. [Jenike, *Storage and Flow of Solids,* Univ. of Utah, *Eng. Exp. Station Bulletin,* no. 123, November (1964). See also Sec. 21 on storage bins, silos, and hoppers.]

Compact Density Compact strength depends on the number and strength of interparticle bonds (Eq. 20-43) created during consolidation, and both generally increase with increasing compact density. Compact density is in turn a function of the maximum pressure achieved during compaction. The **mechanisms of compaction** have been discussed by Cooper & Eaton [*J. Am. Ceramic Soc.,* **45,** 97 (1962)] in terms of two largely independent, probabilistic processes. The first is the filling of large holes with particles from the original size distribution. The second is the filling of holes smaller than the original particles by **plastic flow** or **fragmentation.** Additional, possible mechanisms include the low pressure elimination of arches and cavities created during die filling due to wall effects, and the final high-pressure consolidation of the particle phase itself. As these mechanisms manifest themselves over different pressure ranges, four stages of compression are generally observed in the compressibility diagram when density is measured over a wide pressure range (Fig. 20-77). The slope of the intermediate- and high-pressure regions is defined as $1/\kappa$ where κ is the **compressibility** of the powder. The density at an arbitrary pressure σ is given by a compaction equation of the form

$$\rho = \rho_0 \left[\frac{\sigma}{\sigma_0} \right]^{1/\kappa} \qquad (20\text{-}65)$$

where ρ_0 is the density at an arbitrary pressure or stress σ_0. For a complete review of compaction equations, see Kawakita & Lüdde [*Powder Tech.,* **4,** 61 (1970/71)] and Hersey et al. [*Proceedings of First International Conf. of Compaction & Consolidation of Particulate Matter,* Brighton, 165 (1972)].

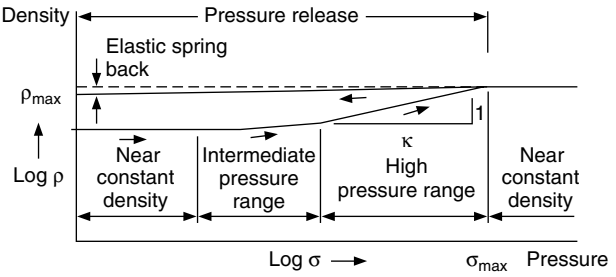


FIG. 20-77 Compressibility diagram of a typical powder illustrating four stages of compaction.

Transmission of Forces As pressure is applied to a powder in a die or roll press, various zones in the compact are subjected to differing intensities of pressure and shear. Compaction stress decreases with axial distance from the applied pressure [Strijbos *et al., Powder Tech.,* **18,** 187 & 209 (1977)] due to **frictional properties** of the powder and die wall. For example, the axial pressure experienced within a cylindrical die with an applied axial load σ_0 may be estimated to a first approximation by

$$\sigma_z = \sigma_0 e^{-(4\mu_w \lambda_\phi / D)z} \qquad (20\text{-}66)$$

where D is die diameter, z is axial distance from the applied load, λ is the ratio of radial to axial pressure given by $\lambda \approx K_\phi = (1 - \sin \phi_e)/(1 + \sin \phi_e)$, and μ_w and ϕ_e are the wall friction coefficient and effective angle of friction defined above (Eqs. 20-63 and 64). Typical pressure and density distributions for uniaxial compaction are shown in Fig. 20-78. High- and low-density annuli are apparent along the die corners, with a dense axial core in the lower part of the compact and a low-density core just below the moving upper punch. These density variations are due to the formation of a dense conical wedge acting along the top punch (A) with a resultant force directed toward the center of the compact (B). The wedge is densified to the greatest extent by the shearing forces developed by the axial motion of the upper punch along the stationary wall, whereas the corners along the bottom stationary die are densified the least (C). The lower axial core (B) is densified by the wedge, whereas the upper low-density region (D) is shielded by the wedge from the full axial compressive force. These variations in compact density lead to local variations in strength as well as differential zones of expansion upon compact unloading, which in turn can lead to flaws in the compact.

Compact Strength Both **particle size** and **bond strength** control final compact strength (Eq. 20-43). Although particle surface energy and elastic deformation play a role, **plastic deformation** at particle contacts is likely the major mechanism contributing to large *permanent* bond formation and successful compaction in practice. Figure 20-79 illustrates the strength of mineral compacts of varying hardness and size cut. To obtain significant strength, Benbow [*Enlargement & Compaction of Particulate Solids,* Stanley-Wood (ed.), Butterworths, 169 (1983)] found that a **critical yield pressure** must be exceeded which was independent of size but increased linearly with particle hardness. Strength also increases linearly with compaction pressure, with the slope inversely related to particle size. Similar results were obtained by others for ferrous powder, sucrose, sodium chloride, and coal [Hardman & Lilly, *Proc. Royal Soc. A.,* **333,** 183 (1973)]. Particle hardness and elasticity may be characterized directly by nanoindentation [Johnnson & Ennis, *Proceedings of the First International Particle Technology Forum,* vol. 2, AIChE, Denver, 178 (1994)].

The development of flaws and the loss of interparticle bonding during decompression substantially weaken compacts (see breakage subsection). **Delamination** during load removal involves the fracture of the compact into layers, and it is induced by strain recovery in excess of the elastic limit of the material which cannot be accommodated by

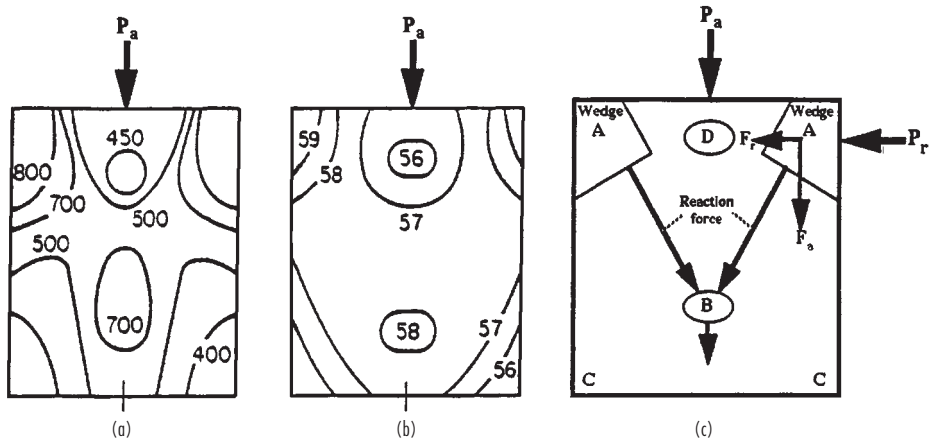


FIG. 20-78 Reaction in compacts of magnesium carbonate when pressed (P_a = 671 kg/cm^2). (*a*) Stress contour levels in kilograms per square centimeter. (*b*) Density contours in percent solids. (*c*) Reaction force developed at wedge responsible for stress and density patterns. [*Train,* Trans. Inst. Chem. Eng. (London), ***35,*** *258 (1957).*]

plastic flow. Delamination also occurs during compact ejection, where the part of the compact which is clear of the die elastically recovers in the radial direction while the lower part remains confined. This differential strain sets up shear stresses causing fracture along the top of the compact referred to as **capping.**

Hiestand Tableting Indices Likelihood of failure during decompression depends on the ability of the material to relieve elastic stress by plastic deformation without undergoing brittle fracture, and this is time dependent. Those which relieve stress rapidly are less likely to cap or delaminate. Hiestand & Smith [*Powder Tech.,* **38,** 145 (1984)] developed three pharmaceutical **tableting indices,** which are applicable for general characterization of powder compactability. The **strain index** (SI) is a measure of the elastic recovery following plastic deformation, the **bonding index** (BI) is a measure of plastic deformation at contacts and bond survival, and the **brittle fracture index** (BFI) is a measure of compact brittleness.

Compaction Cycles Insight into compaction performance is gained from direct analysis of pressure/density data over the cycle of

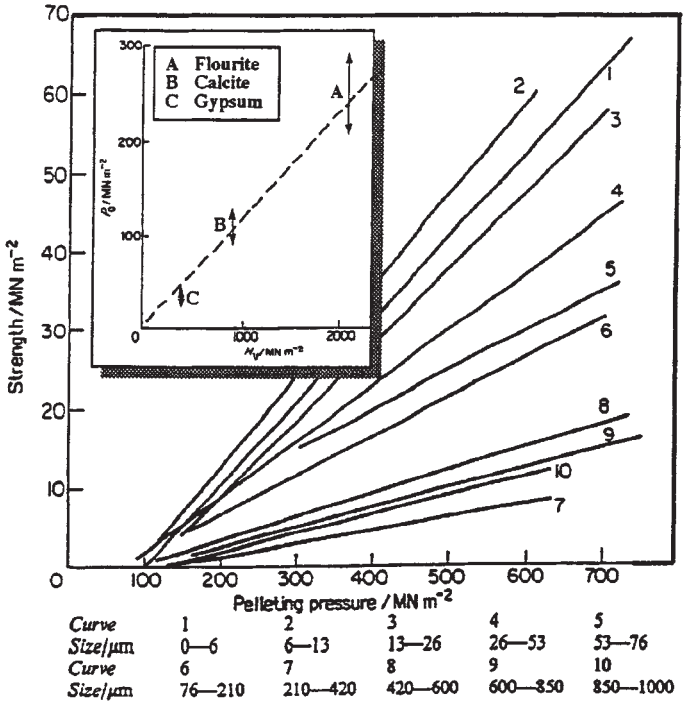


FIG. 20-79 Effect of pelleting pressure on axial crushing strength of compacted calcite particles of different sizes demonstrating existence of a critical yield pressure. Inset shows the effect of hardness on critical yield pressure. [*Benbow,* Enlargement and Compaction of Particulate Solids, *Stanley-Wood (ed.), Butterworths, 169 (1983).*]

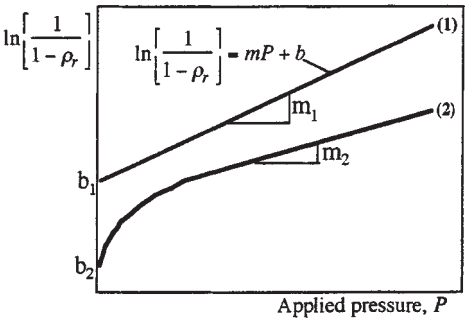


FIG. 20-80 Heckel profiles of the unloaded relative compact density for (1) a material densifying by pure plastic deformation, and (2) a material densifying with contributions from brittle fragmentation and particle rearrangement.

axial compact compression and decompression. Figure 20-80 illustrates typical **Heckel profiles** for plastic and brittle deforming materials which are determined from density measurements of *unloading* compacts. The slope of the curves gives an indication of the yield pressure of the particles. The contribution of fragmentation and rearrangement to densification is indicated by the low-pressure deviation from linearity. In addition, elastic recovery contributes to the degree of hysterisis which occurs in the *at-pressure* density curve during compression followed by decompression. [Doelker, *Powder Technology & Pharmaceutical Processes,* Chulia et al. (eds.), Elsevier, 403 (1994).]

Powder Feeding Bulk density control of feed materials and reproducible powder feeding are crucial to the smooth operation of compaction techniques. In the case of pharmaceutical tableting, reproducible tablet weights with variations of less than 2 percent are required. Feeding problems are most acute for direct powder-filling of compression devices, as opposed to granular feeds. **Flowability data** developed from shear cell measurements are invaluable in designing machine hoppers for device filling. In addition, complex-force feeding systems have been developed to aid filling and ensure uniform bulk density. Lubricants or glidants such as fumed silica and talc are also added in small amounts to improve flow properties. These additives act to modify coefficients of friction of the particulate feed.

Controlling Powder Compaction Compaction properties of powders are generally improved by altering flow properties. In particular, stress transmission improves with either low wall-friction angle or raising the internal angle of friction of the powder. **Internal lubricants** may be mixed with the feed material to be compacted. They may aid stress transmission by reducing the wall angle of friction angle of the material, but may also weaken bonding properties and the unconfined yield stress of the powder. **External lubricants** are applied to the die surface. They reduce sticking to the die and aid stress transmission by reducing the wall angle of friction of the material.

Binders improve the strength of compacts through increased plastic deformation or chemical bonding. They may be classified as **matrix type, film type,** and **chemical.** Komarek [*Chem. Eng.,* **74**(25), 154 (1967)] provides a classification of binders and lubricants used in the tableting of various materials.

Particle properties such as size, shape, elastic/plastic properties, and surface properties are equally important. Their direct effect, however, is difficult to ascertain without thorough particle characterization. Generally, friction coefficients decrease with decreasing particle hardness. Increasing particle size and decreasing the spread of the size distribution lowers powder friction, thereby aiding stress transmission. However, increasing particle size may also lower compact strength, as described by Eq. (20-43).

SIZE ENLARGEMENT EQUIPMENT AND PRACTICE

GENERAL REFERENCES: Ball et al., *Agglomeration of Iron Ores,* Heinemann, London, 1973. Capes, *Particle Size Enlargement,* Elsevier, New York, 1980. Ennis & Litster, *The Science & Engineering of Granulation Processes,* Blackie Academic Ltd., 1997. Knepper (ed.) *Agglomeration,* Interscience, New York, 1962. Kristensen, *Acta Pharm. Suec.,* **25,** 187, 1988. Pietsch, *Size Enlargement by Agglomeration,* John Wiley & Sons Ltd., Chichester, 1992. Pietsch, *Roll Pressing,* Heyden, London, 1976. Sastry (ed.), *Agglomeration 77,* AIME, New York, 1977. Sherrington & Oliver, *Granulation,* Heyden, London, 1981. Stanley-Wood, *Enlargement and Compaction of Particulate Solids,* Butterworth & Co. Ltd., 1983.

Particle size enlargement equipment can be classified into several groups, with advantages, disadvantages, and applications summarized in Table 20-36. Comparisons of bed-agitation intensity, compaction pressures, and product bulk density for selected agglomeration processes are highlighted above in Fig. 20-71.

Particle size terminology is industry specific. In the following discussion, particle size enlargement in tumbling, mixer and fluidized-bed granulators is referred to as **granulation.** Granulation includes **pelletization** or **balling** as used in the iron-ore industry, but does not include the breakdown of compacts as used in some tableting industries. The term pelleting or pelletization will be used for extrusion processes only.

TUMBLING GRANULATORS

In **tumbling granulators,** particles are set in motion by the tumbling action caused by the balance between gravity and centrifugal forces. The most common types of tumbling granulators are **disc** and **drum** granulators. Their use is widespread, including the iron-ore industry (where the process is sometimes called **balling** or **wet pelletization**), fertilizer manufacture, agricultural chemicals and pharmaceuticals.

Tumbling granulators generally produce granules in the size range 1 to 20 mm and are not suitable for making granules smaller than 1 mm. Granule density generally falls between that of fluidized-bed and mixer granulators (Fig. 20-71), and it is difficult to produce highly porous agglomerates in tumbling granulators. Tumbling equipment is also suitable for coating large particles, but it is difficult to coat small particles, as growth by coalescence of the seed particles is hard to control.

Drum and disc granulators generally operate in **continuous feed** mode. A key advantage to these systems is the ability to run at large scale. Drums with diameters up to four meters and throughputs up to 100 ton/hr are widely used in the mineral industry.

Disc Granulators Figure 20-81 shows the elements of a **disc granulator.** It is also referred to as a **pelletizer** in the iron-ore industry or a **pan granulator** in the agricultural chemical industry. The equipment consists of a rotating, tilted disc or pan with a rim. Solids and wetting agents are continuously added to the disc. A coating of the feed material builds up on the disc and the thickness of this layer is controlled by scrapers or a plow, which may oscillate mechanically. The surface of the pan may also be lined with expanded metal or an abrasive coating to promote proper lifting and cascading of the particulate bed, although this is generally unnecessary for fine materials. Solids are typically fed by either volumetric or gravimetric feeders. Gravimetric feeding generally improves granulation performance due to smaller fluctuations in feed rates which act to disrupt rolling action in the pan. Wetting fluids which promote growth are generally applied by a series of single-fluid spray nozzles distributed across the face of the bed. Solids feed and spray nozzle locations have a pronounced effect on granulation performance and granule structure.

Variations of the simple pan shape include (1) an outer reroll ring which allows granules to be simultaneously coated or densified without further growth, (2) multistepped sidewalls, and (3) a pan in the form of a truncated cone (Capes, *Particle Size Enlargement,* Elsevier, 1980).

The required disc-rotation speed is given in terms of the **critical speed,** i.e., the speed at which a single particle is held stationary on

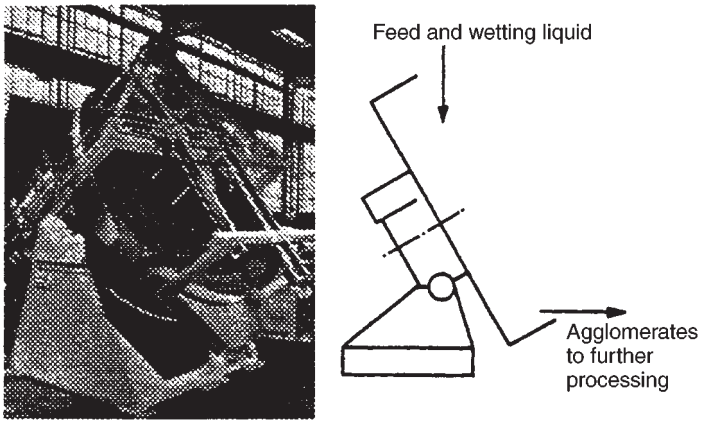


FIG. 20-81 A typical disc granulator (*Capes,* Particle Size Enlargement, *Elsevier, 1980*).

the rim of the disc due to centripetal forces. The critical speed N_c is given by:

$$N_c = \sqrt{\frac{g \sin \phi}{2\pi^2 D}} \qquad (20\text{-}67)$$

where g is the gravitational acceleration, ϕ is the angle of the disc to the horizontal, and D is the disc diameter. The typical operating range for discs is 50 to 75 percent of critical speed, with angles ϕ of 45–55°. This range ensures a good tumbling action. If the speed is too low, sliding will occur. If the speed is too high, particles will be thrown off the disc or openings develop in the bed, allowing spray blowthrough and uneven buildup on the disc bottom. Proper speed is influenced by flow properties of the feed materials in addition to granulation performance.

Discs range in size from laboratory models 30 cm in diameter up to production units of 10 meters in diameter with throughputs of 100 ton/hr. Figure 20-82 shows throughput capacities for discs of varying diameter for different applications and formulation feed densities. When scaling up from laboratory or pilot tests it is usual to keep the same disc angle and fraction of critical speed. Power consumption and throughput are approximately proportional to the square of disc diameter, and disc height is typically 10-20 percent of diameter. It should be emphasized that these relationships are best used as a guide and in combination with actual experimental data on the system in question in order to indicate the approximate effect of scale-up.

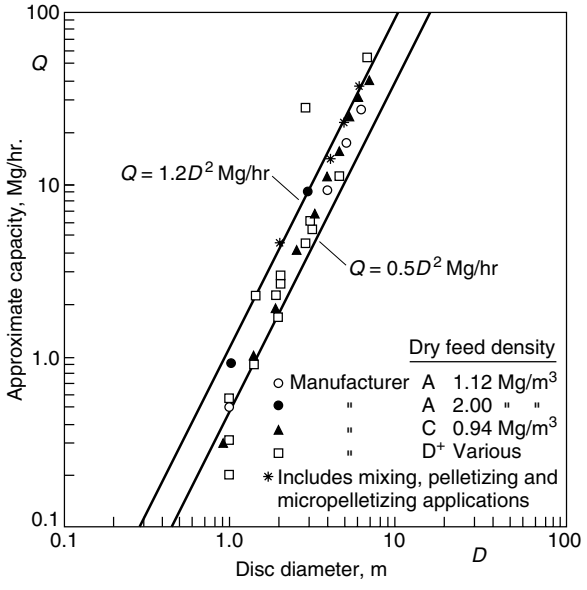


FIG. 20-82 Capacity of inclined disc granulators of varying diameter and formulation feed densities. (*Capes,* Particle Size Enlargement, *Elsevier, 1980.*)

A key feature of disc operation is the inherent **size classification** (Fig. 20-83). Product overflows from the **eye** of the tumbling granules where the large granules are segregated. The overflow size distribution is narrow compared to drum granulators, and discs typically operate with little or no pellet recycle. Due to this segregation, positioning of the feed and spray nozzles is key in controlling the balance of granulation-rate processes.

Total holdup and granule residence time distribution vary with changes to operating parameters which affect granule motion on the disc. Total holdup (mean residence time) increases with decreasing pan angle, increasing speed and increasing moisture content. The residence time distribution for a disc lies between the mixing extremes of plug flow and completely mixed. Increasing the disc angle narrows the residence time distribution. Several mixing models for disc granulators have been proposed (see Table 20-58 in modeling and simulation subsection). One to two-minute residence times are common.

Drum Granulators **Granulation drums** are common in the metallurgical and fertilizer industries and are primarily used for very large throughput applications (see Table 20-43). In contrast to discs, there is no output size classification and high recycle rates of off-size product are common. As a first approximation, granules can be considered to flow through the drum in plug flow, although backmixing to some extent is common.

A granulation drum consists of an inclined cylinder which may be either open-ended or fitted with annular retaining rings. Feeds may

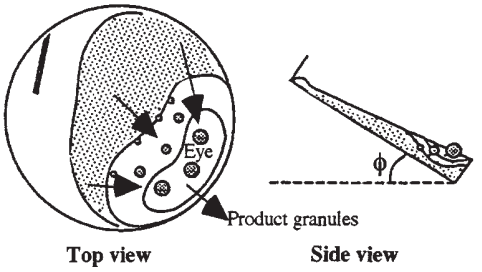


FIG. 20-83 Granule segregation on a disc granulator, illustrating a size-classified granular bed sitting on ungranulated feed powder. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries*, Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

TABLE 20-43 Characteristics of Large-Scale Granulation Drums*

Diameter, (ft)	Length, (ft)	Power, (hp)	Speed, (rpm)	Approximate capacity, (ton/hr)†
Fertilizer granulation				
5	10	15	10–17	7.5
6	12	25	9–16	10
7	14	30	9–15	20
8	14	60	20–14	25
8	16	75	20–14	40
10	20	150	7–12	50
Iron-ore balling				
9	31	60	12–14	54
10	31	60	12–14	65
12	33	75	10	98

*Capes, *Particle Size Enlargement,* Elsevier (1980)
†Capacity excludes recycle. Actual drum throughput may be much higher.
NOTE: To convert feet to centimeters, multiply by 30.48; to convert tons/hr to megagrams per hour, multiply by 0.907; and to convert horsepower to kilowatts, multiply by 0.746.

be either premoistened by mixers to form granule nuclei, or liquid may be sprayed onto the tumbling bed via nozzles or distributor-pipe systems. Drums are usually tilted longitudinally a few degrees from the horizontal (0–10°) to assist flow of granules through the drum. The critical speed for the drum is calculated from Eq. 20-67 with ϕ = 80–90°. To achieve a cascading, tumbling motion of the load, drums operate at lower fractions of critical speed than discs, typically 30–50% of N_c. Scrapers of various designs are often employed to control buildup of the drum wall. Holdup in the drum is between 10 and 20% of the drum volume. Drum length ranges from 2–5 times diameter, and power and capacity scale with drum volume. Holdup and mean residence time are controlled by drum length, with difficult systems requiring longer residence times than those that agglomerate readily. One to five-minute residence times are common.

A variation of the basic cylindrical shape is the multicone drum which contains a series of compartments formed by annular baffles [Stirling, in Knepper (ed.), *Agglomeration,* Interscience, New York, 1962].

Drum granulation plants often have significant recycle of undersize, and sometimes crushed oversize granules. Recycle ratios between 2:1 and 5:1 are common in iron-ore balling and fertilizer granulation circuits. This large recycle stream has a major effect on circuit operation, stability, and control. A surge of material in the recycle stream affects both the moisture content and the size distribution in the drum. Surging and limit-cycle behavior are common. There are several possible reasons for this, including:

1. A shift in controlling mechanism from coalescence to layering when the ratio of recycled pellets to new feed changes [Sastry and Fuerstenau, *Trans. Soc. Mining Eng.,* AIME, **258,** 335–340 (1975)].
2. Significant changes in the moisture content in the drum due to recycle fluctuations (recycle of dry granules in fertilizer granulation) [Zhang et al., *Control of Particulate Processes IV* (1995)].

In many cases, plants simply live with these problems. However, use of modern model-based control schemes in conjunction with improved methods for on-line moisture and particle size analysis can help overcome these effects [Ennis (ed.), *Powder Tech.,* **82** (1995); Zhang et al., *Control of Particulate Processes IV* (1995)].

Granulation Rate Processes and Effect of Operating Variables Granulation rate processes have been discussed in detail above (see "Agglomeration Rate Processes"). Nucleation, coalescence, consolidation, and layering are all important processes in tumbling granulation. In tumbling granulators, the growth processes are complex for a number of reasons:

1. Granules remain wet and can deform and consolidate. The behavior of a granule is therefore a function of its history.
2. Different granulation behavior is observed for broad- and narrow-size distributions.
3. There is often complex competition between growth mechanisms.

Consolidation of the granules in tumbling granulators directly determines granule density and porosity. Since there is typically no in situ drying to stop the consolidation process, granules consolidate over extended times. Increasing size, speed, and angle of drums and discs will increase the rate of consolidation. Increasing residence time through lower feed rates will increase the extent of consolidation. With disc granulators, residence time can also be increased by increasing bed depth (controlled by bottom inserts), raising disc speed, or lowering disc angle. With drum granulators, residence time can be influenced by internal baffling.

Growth rate is very sensitive to liquid content for narrow initial-size distributions, with increases in liquid content for fine powders leading to an approximate exponential increase in granule size. For low-viscosity liquids, granulation occurs when very close to the saturation of the granule. This leads to the following equation to estimate moisture requirements [Capes, *Particle Size Enlargement,* Elsevier (1980)]:

$$w = \frac{\varepsilon\rho_l}{\varepsilon\rho_l + (1-\varepsilon)\rho_s}$$

$$w = \frac{1}{1 + 1.85(\rho_s/\rho_l)};\ d_p < 30\ \mu\text{m} \qquad (20\text{-}68)$$

$$w = \frac{1}{1 + 2.17(\rho_s/\rho_l)};\ d_p > 30\ \mu\text{m}$$

where w is the weight fraction of the liquid, ε is the porosity of the close-packed material, ρ_s is true particle density, ρ_l is liquid density, and d_p is the average size of the feed material. Equation (20-68) is suitable for preliminary mass-balance requirements for liquid binders with similar properties to water. If possible, however, the liquid requirements should be measured in a balling test on the material in question, since unusual packing and wetting effects, particle internal porosity, and solubility, air inclusions, etc. may cause error. Approximate moisture requirements for balling several materials are given in Table 20-44. In addition, for materials containing soluble constituents, such as fertilizer formulations, the total solution-phase ratio controls growth, and not simply the amount of binding fluid used.

When fines are recycled, as in iron ore, sinter feed, or fertilizer drum granulation, they are rapidly granulated and removed from the

TABLE 20-44 Moisture Requirements for Granulating Various Materials

Raw material	Approximate size of raw material, less than indicated mesh	Moisture content of balled product, wt % H_2O
Precipitated calcium carbonate	200	29.5–32.1
Hydrated lime	325	25.7–26.6
Pulverized coal	48	20.8–22.1
Calcined ammonium metavanadate	200	20.9–21.8
Lead-zinc concentrate	20	6.9–7.2
Iron pyrite calcine	100	12.2–12.8
Specular hematite concentrate	150	8.0–10.0
Taconite concentrate	150	8.7–10.1
Magnetic concentrate	325	9.8–10.2
Direct-shipping open-pit iron ores	10	10.3–10.9
Underground iron ore	¼ in.	10.4–10.7
Basic oxygen converter fume	1 μ	9.2–9.6
Raw cement meal	150	13.0–13.9
Fly ash	150	24.9–25.8
Fly ash-sewage sludge composite	150	25.7–27.1
Fly ash-clay slurry composite	150	22.4–24.9
Coal-limestone composite	100	21.3–22.8
Coal-iron ore composite	48	12.8–13.9
Iron ore-limestone composite	100	9.7–10.9
Coal-iron ore-limestone composite	14	13.3–14.8

*Dravo Corp.

distribution up to some critical size, which is a function of both moisture content and binder viscosity. Changing the initial-size distribution changes the granule porosity and hence moisture requirements [Adetayo et al., *Chem. Eng. Sci.*, **48,** 3951 (1993)]. Since recycle rates in drum systems are high, differences in size distribution between feed and recycle streams are one source of the limit-cycle behavior observed in practice.

Growth by layering is important for the addition of fine powder feed to recycled well-formed granules in drum granulation circuits and for disc granulators. In each case, layering will compete with nuclei formation and coalescence as growth mechanisms. Layered growth leads to a smaller number of larger, denser granules with a narrower-size distribution than growth by coalescence. Layering is favored by a high ratio of pellets to new feed, low moisture and positioning powder feed to fall onto tumbling granules.

Granulator-Dryers for Layering and Coating Some designs of tumbling granulators also act as dryers specifically to encourage layered growth or coating and discourage coalescence or agglomeration, e.g., the fluidized-drum granulator [Anon, *Nitrogen*, **196,** 3–6 (1992)]. These systems have drum internals designed to produce a falling curtain of granules past an atomized feed solution or slurry. Layered granules are dried by a stream of warm air before circulating through the coating zone again. Applications are in fertilizer and industrial chemicals manufacture. Analysis of these systems is similar to fluidized-bed granulator dryers.

In the pharmaceutical industry, pan granulators are still widely used for coating application. Pans are suitable for coating only relatively large granules or tablets. For smaller particles, the probability of coalescence is too high.

Relative Merits of Disc versus Drum Granulators The principal difference between disc and drum granulators is the classifying action of the disc, resulting in disc granulators having narrower exit-granule-size distributions than drums. This alleviates the need for product screening and recycle for disc granulators in some industries with only moderate-size specifications. For industries with tighter specifications, however, recycle rates are rarely more than 1:2 compared to drum recycle rates often as high as 5:1. The classified mixing action of the disc affects product bulk density, growth mechanisms, and granule structure as well. Generally, drum granulators produce denser granules than discs. Control of growth mechanisms on discs is complex, since regions of growth overlap and mechanisms compete. Both layered and partially agglomerated structures are therefore possible in disc granulators.

Other advantages claimed for the disc granulator include low equipment cost, sensitivity to operating controls, and easy observation of the granulation/classification action, all of which lend versatility in agglomerating many different materials. Dusty materials and chemical reactions such as the ammoniation of fertilizer are handled less readily in the disc granulator than in the drum.

Advantages claimed for the drum granulator over the disc are greater capacity, longer retention time for materials difficult to agglomerate or of poor flow properties, and less sensitivity to upsets in the system due to the damping effect of a large, recirculated load. Disadvantages are high recycle rates which can promote limit-cycle behavior or degradation of properties of the product.

MIXER GRANULATORS

Mixer granulators contain an agitator to mix particles and liquid to cause granulation. In fact, mixing any wet solid will cause some granulation, even if unintentionally. Mixer granulators have a wide range of applications including pharmaceutical, agrochemical, and detergent (Table 20-36), and they have the following advantages:

- They can process plastic, sticky materials.
- They can spread viscous binders.
- They are less sensitive to operating conditions than tumbling granulators.
- They can produce small (<2 mm) high-density granules.

Power and maintenance costs are higher than for tumbling granulators. Outside of high-intensity continuous systems (e.g., the Schugi in-line mixer), mixers are not feasible for very large throughput applications if substantial growth is required. Granules produced in mixer granulators may not be as spherical as those produced in tumbling granulators, and are generally denser due to higher-agitation intensity (see Fig. 20-71). Control of the amount of liquid phase and the intensity and duration of mixing determine agglomerate size and density. Due to greater compaction and kneading action, generally less liquid phase is required in mixers than in tumbling granulation.

Low-Speed Mixers **Pug mills** and **paddle mills** are used for both batch and continuous applications. These devices have horizontal troughs in which rotate central shafts with attached mixing blades of bar, rod, paddle, and other designs. (See Sec. 19.) The vessel may be of single- or double-trough design. The rotating blades throw material forward and to the center to achieve a kneading, mixing action. Characteristics of a range of pug mills available for fertilizer granulation are given in Table 20-45. These mills have largely been replaced by tumbling granulators in metallurgical and fertilizer applications, but they are still used as a premixing step for blending very different raw materials e.g., filter cake with dry powder.

Batch planetary mixers are used extensively in the pharmaceutical industry for powder granulation. A typical batch size of 100 to 200 kg has a power input of 10 to 20 kW. Mixing times in these granulators are quite long (20 to 40 min).

High-Speed Mixers **High-speed mixers** include continuous-shaft mixers and batch high-speed mixers. **Continuous-shaft mixers** have blades or pins rotating at high speed on a central shaft. Both horizontal and vertical shaft designs are available. Examples include the vertical **Schugi mixer** (Fig. 20-84) and the horizontal **pin** or **peg**

TABLE 20-45 Characteristics of Pug Mixers for Fertilizer Granulation*

Model	Material bulk density, lb/ft^3	Approximate capacity, tons/h	Size (width × length), ft	Plate thickness, in	Shaft diameter, in	Speed, r/min	Drive, hp
A	25	8	2 × 8	¼	3	56	15
	50	15	2 × 8	¼	3	56	20
	75	22	2 × 8	¼	3	56	25
	100	30	2 × 8	¼	3	56	30
B	25	30	4 × 8	⅜	4	56	30
	50	60	4 × 8	⅜	4	56	50
	75	90	4 × 8	⅜	4	56	75
	100	120	4 × 8	⅜	5	56	100
C	25	30	4 × 12	⅜	5	56	50
	50	60	4 × 12	⅜	5	56	100
	75	90	4 × 12	⅜	6	56	150
	100	120	4 × 12	⅜	6	56	200
	125	180	4 × 12	⅜	7	56	300

*Feeco International, Inc. To convert pounds per cubic foot to kilograms per cubic meter, multiply by 16; to convert tons per hour to megagrams per hour, multiply by 0.907; to convert feet to centimeters, multiply by 30.5; to convert inches to centimeters, multiply by 2.54; and to convert horsepower to kilowatts, multiply by 0.746.

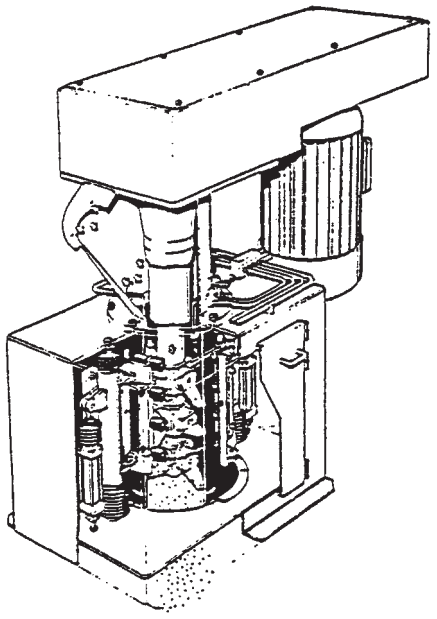


FIG. 20-84 The Schugi Flexomix® vertical high-shear continuous granulator. Shaft speeds range from 100–3500 rpm, capacities from 0.1 to 200 megagrams per hour, and power requirements from 1–100 kW. (*Courtesy of Hosokawa Micron Australia Pty. Ltd.*)

mixers. These mixers operate at high speed (200 to 3500 rpm) to produce granules of size 0.5 to 1.5 mm with a residence time of a few seconds. Schugi capacities may range up to 50 tons/hr. Typical plant capacities of lower-shear peg mixers are 10-20 tons/hr [Capes, *Particle Size Enlargement*, 1980]. Examples of applications include detergents, agricultural chemicals, clays, ceramics, and carbon black.

Batch high-shear mixer granulators are used extensively in the pharmaceutical industry. Plow-shaped mixers rotate on a horizontal shaft at 60 to 800 rpm. Separate high-speed cutters or choppers rotate at much higher speed (500 to 3500 rpm) and are used to limit the maximum granule size. Granulation times of the order 5–10 mins are common, which includes both wet massing and granulation stages operating at low and high impeller speed, respectively. Several designs with both vertical and horizontal shafts are available (Fig. 20-85). Popular designs include horizontal Lödige and vertical Diosna, Fielder, and Gral granulators [Schaefer, *Acta. Pharm. Sci.*, **25,** 205 (1988)].

Granulation-Rate Processes and Effect of Operating Variables Granule deformation is important due to the higher agitation intensity existing in high-shear mixers as compared with tumbling granulators (see Fig. 20-71 and "Growth and Consolidation: High Agitation Intensity Growth"). As deformability is linked to granule saturation and interparticle, frictional forces, consolidation and growth are highly coupled as illustrated in Fig. 20-86 where continued growth is associated with continued compaction and decreases in granule porosity. Impeller shaft power intensity has been used both as a rheological tool to characterize formulation deformability as well as a control technique to judge granulation end-point. [See Kristensen et al., *Acta. Pharm. Sci.*, **25,** 187 (1988) and Holm et al., *Powder Tech.*, **43,** 225 (1985).]

Scale-Up and Operation Scale-up of pharmaceutical mixer granulators is difficult because geometric similarity is often not preserved. Kristensen recommends constant relative swept volume ratio $\dot{V}_R$ as a scale-up parameter defined as:

$$\dot{V}_R = \frac{\dot{V}_{imp}}{V_{tot}} \tag{20-69}$$

where $\dot{V}_{imp}$ is the volume rate swept by the impeller and V_{tot} is the total volume of the granulator. Depending on mixer design, relative swept volume may decrease significantly with scale [Schaefer, loc. cit.] requiring increases in impeller speed with scale-up. In general, scale-up leads to poorer liquid distribution, higher-porosity granules and wider granule-size distributions. Required granulation time may increase with scale, though this depends on the importance of consolidation kinetics as discussed above.

Power dissipation can lead to temperature increases of up to 40°C in the mass. Note that evaporation of liquid as a result of this increase needs to be accounted for in determining liquid requirements for granulation. Liquid should be added through an atomizing nozzle to aid uniform liquid distribution in many cases. In addition, power intensity (kW/kg) has been used with some success to judge granulation end point and for scale-up, primarily due to its relationship to granule deformation [Holm loc. cit.]. Swept volume ratio is a preliminary estimate of expected power intensity.

FLUIDIZED-BED AND RELATED GRANULATORS

In fluidized granulators (**fluidized beds** and **spouted beds**), particles are set in motion by air, rather than by mechanical agitation. Applications include fertilizers, industrial chemicals, agricultural chemicals, pharmaceutical granulation, and a range of coating processes. Fluidized granulators produce either high-porosity granules due to the agglomeration of powder feeds or high-strength layered granules due to coating of seed particles or granules by liquid feeds.

Figure 20-87 shows a typical production-size **batch** fluid-bed granulator. The air-handling unit dehumidifies and heats the inlet air. Heated fluidization air enters the processing zone through a distribu-

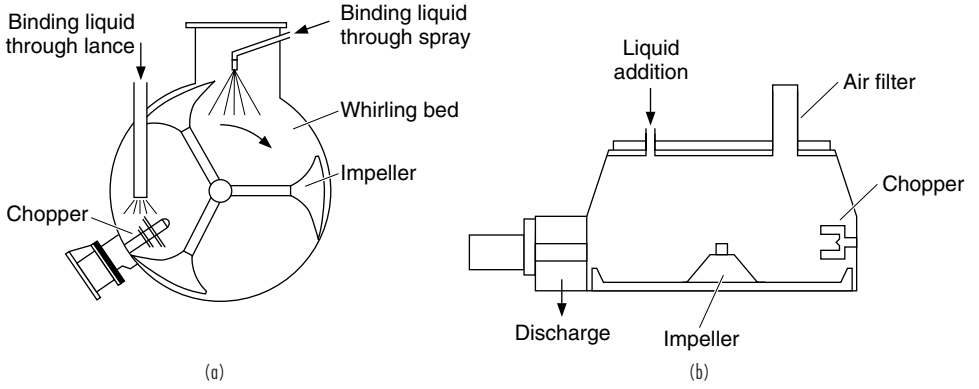


FIG. 20-85 *(a)* Horizontal and *(b)* vertical high-shear mixer granulators for pharmaceutical granule preparation for subsequent tableting.

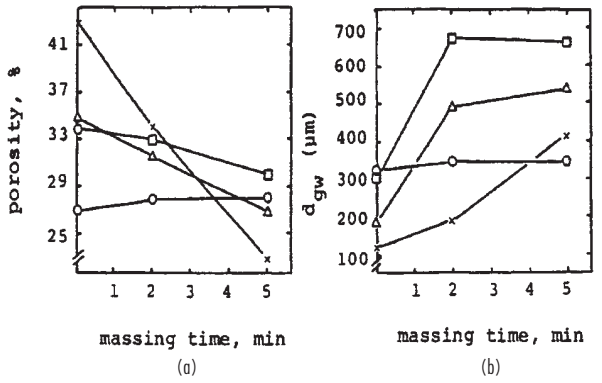


FIG. 20-86 Relationship between consolidation and growth kinetics in high-shear mixer granulators. Effect of wet-massing time on intragranular porosity (*a*) and granule size (*b*) in a high-shear mixer, Fielder PMAT 25 VG. Impeller speed: 250 rpm. Chopper speed: 3000 rpm. Starting materials: Lactose, o; Dicalcium phosphate, x. Dicalcium phosphate/cornstarch 85/15 w/wt %: △. Dicalcium phosphate/cornstarch 55/45 w/wt %: h [*Kristensen et al.*, Acta Pharm. Sci., **25,** *187 (1988).*]

tor which also supports the particle bed. Liquid binder is sprayed through an air-atomizing nozzle located above, in, or below the bed. Bag filters or cyclones are needed to remove dust from the exit air. Other fluidization gases such as nitrogen are also used in place of or in combination with air to avoid potential explosion hazards due to fine powders.

Continuous fluid-bed granulators are used in the fertilizer and detergent industries. For fertilizer applications, near-size granules are recycled to control the granule size distribution. Dust is not recycled directly, but first remelted or slurried in the liquid feed.

Advantages of fluidized-beds over other granulation systems include high-volumetric intensity, simultaneous drying and granulation, high heat and mass-transfer rates, and robustness with respect to operating variables on product quality. Disadvantages include the effect of high operating costs with respect to air handling and dust containment, and the potential of defluidization due to uncontrolled growth.

Hydrodynamics The **hydrodynamics** of fluidized beds is covered in detail in Sec. 17. Only aspects specifically related to particle size enlargement are discussed here. Granular product from fluidized beds are generally **group B** or **group D** particles under Geldart's powder classification. However, for batch granulation, the bed may initially consist of a **group A** powder. For granulation, fluidized beds typically operate in the range $1.5U_{mf} < U < 5U_{mf}$ where U_{mf} is the minimum fluidization velocity and U is the operating superficial gas velocity. For batch granulation, the gas velocity may need to be increased significantly during operation to maintain the velocity in this range as the bed particle size increases.

For group B and D particles, nearly all the excess gas velocity ($U - U_{mf}$) flows as bubbles through the bed. The flow of bubbles controls particle mixing, attrition, and elutriation. Therefore, elutriation and attrition rates are proportional to excess gas velocity. Readers should refer to Sec. 17 for important information and correlations on Geldart's powder classification, minimum fluidization velocity, bubble growth and bed expansion, and elutriation.

Mass and Energy Balances Due to the good mixing and heat-transfer properties of fluidized beds, the exit-gas temperature is assumed to be the same as the bed temperature. Fluidized bed gran-

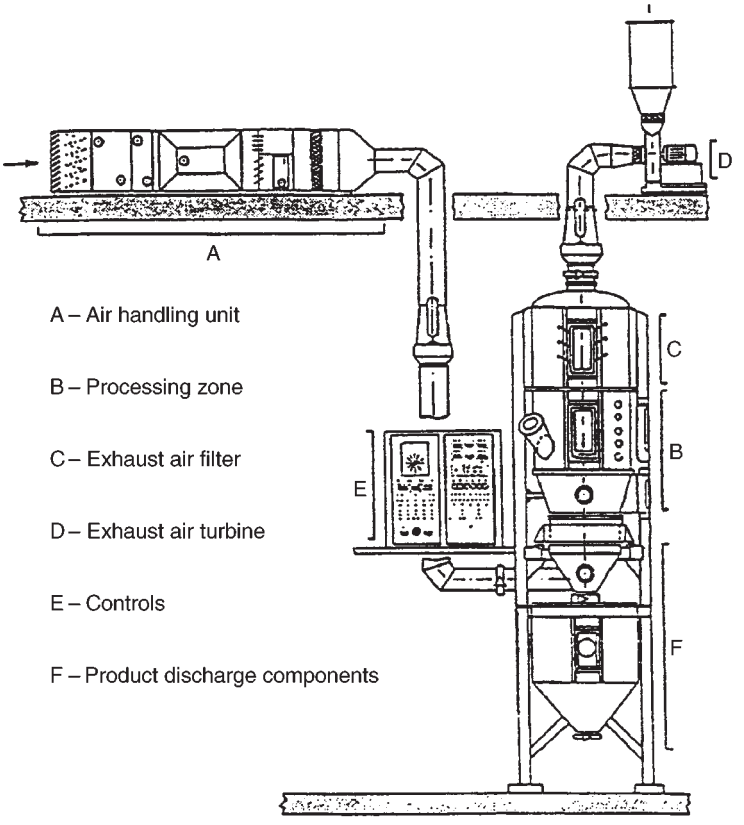


FIG. 20-87 Fluid-bed granulator for batch processing of powder feeds. [*Ghebre-Selassie (ed.),* Pharmaceutical Pelletization Technology, *Marcel Dekker (1989).*]

ulators also act simultaneously as dryers and therefore are subject to the same mass and energy-balance limits as driers, namely:

1. The concentration of solvent of the atomized binding fluid in the exit air cannot exceed the saturation value for the solvent in the fluidizing gas at the bed temperature.
2. The supplied energy in the inlet air must be sufficient to evaporate the solvent and maintain the bed at the desired temperature.

Both these limits restrict the maximum rate of liquid feed or binder addition for given inlet gas velocity and temperature. The liquid feed rate may be further restricted to avoid excess coalescence or quenching.

Granulation Rate Processes and Effect of Operating Variables Table 20-46 summarizes the typical effect of feed properties (material variables) and operating variables on fluidized-bed granulation. Due to the range of mechanisms operating simultaneously, the combined effect of these variables can be complex. "Rules of thumb" for operation are very dependent on knowing the dominant granulation mechanisms or rate processes. Understanding individual rate processes allows at least semiquantitative analysis to be used in design and operation. See Tables 20-38, 20-40, and 20-42 on controlling the individual granulation rate processes of wetting, coalescence and consolidation, and breakage, respectively.

Competing mechanisms of growth include layering which results in dense, strong granules with a very tight size distribution and coalescence which results in raspberrylike agglomerates of higher voidage. Growth rates range from 10–100 $\mu m\ hr^{-1}$ to 100–2000 $\mu m\ hr^{-1}$ for growth by layering and coalescence, respectively.

Air atomizing nozzles are commonly used to control the droplet-size distribution independently of the liquid feed rate and to minimize the chances of **defluidization** due to uncontrolled growth or large droplets.

Equipment Operation **Spray nozzles** suffer from caking on the outside and clogging on the inside. When the nozzle is below the bed surface, fast capture of the liquid drops by bed particles, as well as scouring of the nozzle by particles, prevents caking. Blockages inside the nozzle are also common, particularly for slurries. The nozzle design should be as simple as possible and provision for in situ cleaning or easy removal is essential.

The formation of large, wet agglomerates that dry slowly is called **wet quenching.** Large agglomerates defluidize, causing channeling and poor mixing, ultimately leading to shutdown. Sources of wet quenching include high liquid-spray rates, large spray droplets, or dripping nozzles. **Dry quenching** (uncontrolled coalescence) is the formation and defluidization of large, stable, dry agglomerates, which also may ultimately lead to shutdown. Early detection of quenching is important. The initial stages of defluidization are detected by monitoring the bed temperature just above the distributor. A sudden increase (dry quenching) or decrease (wet quenching) indicates the onset of bed defluidization. Wet quenching is avoided by reducing the liquid feed rate and improving the nozzle operation. In situ jet grinding is sometimes used to limit the maximum stable size of dry agglomerates.

Control is accomplished by monitoring bed temperature, as well as granule size and density of samples. Temperature is controlled best by adjusting the liquid feed rate. For batch granulation, the fluidizing air velocity must be increased during the batch. **Bed pressure fluctuations** can be used to monitor the quality of fluidization and to indicate when gas velocity increases are required. In addition, intermittent sampling systems may be employed with **on-line size analyzers** to monitor granule size. There is no simple heuristic to control the final-granule-size distribution (batch) or exit-granule-size distribution (continuous). A good knowledge of the granulation processes combined with model-based control schemes can be used to fix the batch time (batch), or adjust the seed-granule recycle (continuous) to maintain product quality.

Scale-up of fluid-bed granulators relies heavily on pilot-scale tests. The pilot-plant fluid bed should be at least 0.3 meters in diameter so that bubbling rather than slugging fluidization behavior occurs. Key in scale-up is the increase in agitation intensity with increasing bed height. In particular, granule density and attrition resistance increase linearly with operating bed height whereas the rate of granule dispersion decreases.

Draft Tube Designs and Spouted Beds A **draft tube** is often employed to regulate particle circulation patterns. The most common design is the **Wurster** draft tube fluid bed employed extensively in the pharmaceutical industry, usually for coating and layered growth applications. The **Wurster coater** uses a bottom positioned spray, but other variations are available (Table 20-47).

The **spouted-bed granulator** consists of a central high-velocity **spout** surrounded by a **moving bed annular region.** (See Sec. 17.) All air enters through the orifice at the base of the spout. Particles entrained in the spout are carried to the bed surface and rain down on the annulus as a fountain. Bottom-sprayed designs are the most common. Due to the very high gas velocity in the spout, granules grow by layering only. Therefore, spouted beds are good for coating applications. However, attrition rates are also high, so the technique is not suited to weak granules. Spouted beds are well suited to group D particles and are more tolerant of nonspherical particles than a fluid bed. Particle circulation is better controlled than in a fluidized bed, unless a draft tube design is employed. Spouted beds are difficult to scale past two meters in diameter.

The liquid spray rate to a spouted bed may be limited by agglomerate formation in the spray zone causing spout collapse [Liu & Litster, *Powder Tech.*, **74,** 259 (1993)]. The maximum liquid spray rate increases with increasing gas velocity, increasing bed temperature, and decreasing binder viscosity (see Fig. 20-88). The maximum liquid flow rate is typically between 20 and 90 percent of that required to saturate the exit air, depending on operating conditions. Elutriation of fines from spouted-bed granulators is due mostly to the attrition of newly layered material, rather than spray drying. The elutriation rate is proportional to the kinetic energy in the inlet air (see Eq. 20-71).

TABLE 20-46 Effect of Variables on Fluidized-Bed Granulation*

Operating or material variable	Effect of increasing variable
Liquid feed or spray rate	Increase size and spread of granule-size distribution Increase granule density and strength Increase chance of defluidization due to quenching
Liquid droplet size	Increase size and spread of granule size distribution
Gas velocity	Increase attrition and elutriation rates (major effect) Decrease coalescence for inertial growth No effect on coalescence for noninertial growth Increase granule consolidation and density
Bed height	Increase granule density and strength
Bed temperature	Decrease granule density and strength
Binder viscosity	Increase coalescence for inertial growth No effect on coalescence for noninertial growth Decrease granule density
Particle or granule size	Decrease chance of coalescence Increase required gas velocity to maintain fluidization

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CENTRIFUGAL GRANULATORS

In the pharmaceutical industry, a range of centrifugal granulator designs are used. In each of these, a horizontal disc rotates at high speed causing the feed to form a rotating **rope** at the walls of the

TABLE 20-47 Sizes & Capacities of Wurster Coaters*

Bed diameter, inches	Batch size, kg
7	3–5
9	7–10
12	12–20
18	35–55
24	95–125
32	200–275
46	400–575

*Ghebre-Sellasie (ed.), *Pharmaceutical Pelletization Technology,* Marcel Dekker (1989).

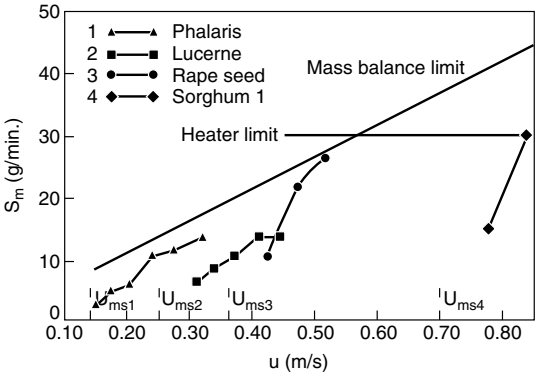


FIG. 20-88 Effect of gas velocity on maximum liquid rate for a spouted-bed seed coater. [*Liu & Litster,* Powder Tech., ***74,*** *259 (1993).*] With kind permission from Elsevier Science SA, Lausanne, Switzerland.

vessel (see Fig. 20-89). There is usually an allowance for drying air to enter around the edge of the spinning disc. Applications of such granulators include spheronization of extruded pellets, dry-powder layering of granules or sugar spheres, and coating of pellets or granules by liquid feeds.

Centrifugal Designs Centrifugal granulators tend to give denser granules or powder layers than fluidized beds and more spherical granules than mixer granulators. Operating costs are reasonable but capital cost is generally high compared to other options. Several types are available including the **CF granulator** (Fig. 20-89) and **rotary fluidized-bed** designs which allow high gas volumes and therefore significant drying rates (Table 20-48). CF granulator capacities range from 3–80 kg with rotor diameters of .36–1.3 meters and rotor speeds of 45–360 rpm [Ghebre-Selassie (ed.), *Pharmaceutical Pelletization Technology,* Marcel Dekker, (1989)].

Particle Motion and Scale-Up Very little fundamental information is published on centrifugal granulators. Qualitatively, good operation relies on maintaining a smoothly rotating **stable rope** of tumbling particles. Operating variables which affect the particle motion are disc speed, peripheral air velocity, and the presence of baffles.

For a given design, good rope formation is only possible for a small range of disc speeds. If the speed is too low, a rope does not form. If the speed is too high, very high attrition rates can occur. Scale-up on the basis of either **constant peripheral speed** (DN = const.), or **constant Froude number** (DN^2 = const.) is possible. Increasing peripheral air velocity and baffles helps to increase the rate of rope turnover. In designs with tangential powder or liquid feed tubes, additional baffles are usually not necessary. The motion of particles in the equipment is also a function of the frictional properties of the feed, so the optimum operating conditions are feed specific.

Granulation Rate Processes Possible granulation processes occurring in centrifugal granulators are extrudate breakage, consolidation, rounding (spheronization), coalescence, powder layering and coating, and attrition. Very little information is available about these processes as they occur in centrifugal granulators, however, similar principles from tumbling and fluid-bed granulators will apply.

SPRAY PROCESSES

Spray processes include **spray driers, prilling towers,** and **flash driers.** Feed solids in a fluid state (solution, gel, paste, emulsion, slurry, or melt) are dispersed in a gas and converted to granular solid products by heat and/or mass transfer. In spray processes, the size distribution of the particulate product is largely set by the drop size distribution, i.e., **nucleation** is the dominant granulation process. Exceptions are where fines are recycled to coalesce with new spray droplets and where spray-dried powders are rewet in a second tower to encourage agglomeration. For spray drying, a large amount of solvent must be evaporated whereas prilling is a spray-cooling process. Fluidized or spouted bed must be used to capture nucleated fines as hybrid granulator designs, e.g., the **fluid-bed spray dryer.**

Product diameter is small and bulk density is low in most cases, except prilling. Feed liquids must be pumpable and capable of atomization or dispersion. Attrition is usually high, requiring fines recycle or recovery. Given the importance of the droplet-size distribution, nozzle design and an understanding of the fluid mechanics of drop formation are critical. In addition, heat and mass-transfer rates during

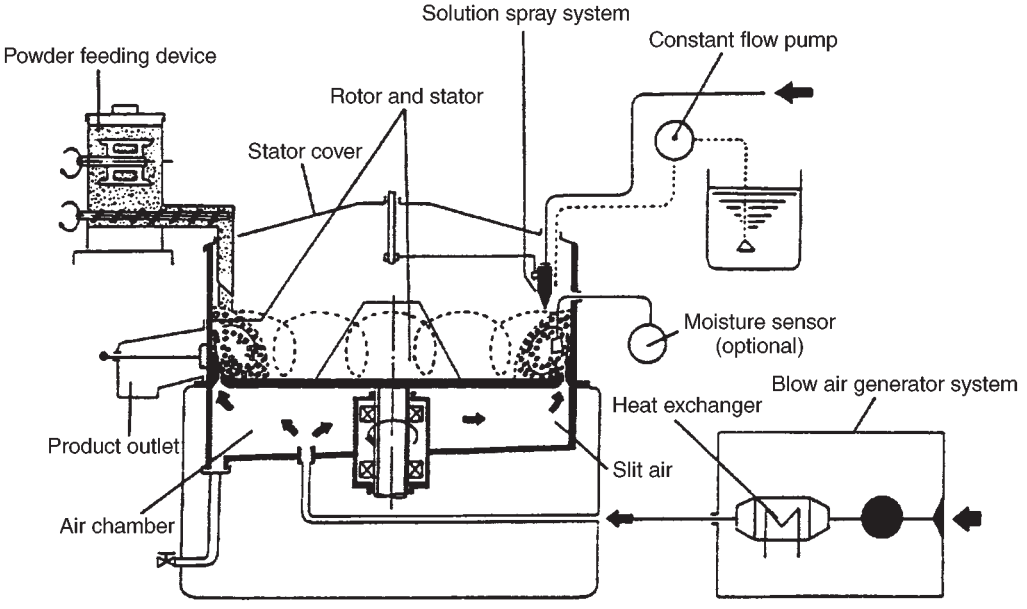


FIG. 20-89 Schematic of a CF granulator. [*Ghebre-Selassie (ed.),* Pharmaceutical Pelletization Technology, *Marcel Dekker (1989).*]

TABLE 20-48 Specifications of Glatt Rotary Fluid-Bed Granulators*

Parameter	15	60	200	500
Volume, liters	45	220	670	1560
Fan				
Power, kW	11	22	37	55
Capacity, m^3/hr	1500	4500	8000	12000
Heating capacity, kW	37	107	212	370
Diameter, m	1.7	2.5	3.45	4.0

*Glatt Company, in Ghebre-Selassie (ed.), *Pharmaceutical Pelletization Technology,* Marcel Dekker (1989).

drying can strongly effect the particle morphology, of which a wide range of characteristics are possible.

Spray Drying Detailed descriptions of spray dispersion dryers, together with application, design, and cost information, are given in Sec. 17. Product quality is determined by a number of properties such as particle form, size, flavor, color, and heat stability. Particle size and size distribution, of course, are of greatest interest from the point of view of size enlargement.

In general, particle size is a function of atomizer-operating conditions and also of the solids content, liquid viscosity, liquid density, and feed rate. Coarser, more granular products can be made by increasing viscosity (through greater solids content, lower temperature, etc.), by increasing feed rate, and by the presence of binders to produce more agglomeration of semidry droplets. Less-intense atomization and spray-air contact also increase particle size, as does a lower exit temperature, which yields a moister (and hence a more coherent) product. This latter type of spray-drying agglomeration system has been described by Masters and Stoltze [*Food Eng.,* 64 (February 1973)] for the production of instant skim-milk powders in which the completion of drying and cooling takes place in vibrating conveyors (see Sec. 17) downstream of the spray dryer.

Prilling The prilling process is similar to spray drying and consists of spraying droplets of liquid into the top of a tower and allowing these to fall against a countercurrent stream of air. During their fall the droplets are solidified into approximately spherical particles or prills which are up to about 3 mm in diameter, or larger than those formed in spray drying. The process also differs from spray drying since the droplets are formed from a melt which solidifies primarily by cooling with little, if any, contribution from drying. Traditionally, ammonium nitrate, urea, and other materials of low viscosity and melting point and high surface tension have been treated in this way. Improvements in the process now allow viscous and high-melting point materials and slurries containing undissolved solids to be treated as well.

The design of a prilling unit first must take into account the properties of the material and its sprayability before the tower design can proceed. By using data on the melting point, viscosity, surface tension, etc., of the material, together with laboratory-scale spraying tests, it is possible to specify optimum temperature, pressure, and orifice size for the required prill size and quality. Tower sizing basically consists of specifying the cross-sectional area and the height of fall. The former is determined primarily by the number of spray nozzles necessary for the desired production rate. Tower height must be sufficient to accomplish solidification and is dependent on the heat-transfer characteristics of the prills and the operating conditions (e.g., air temperature). Because of relatively large prill size, narrow but very tall towers are used to ensure that the prills are sufficiently solid when they reach the bottom. Table 20-49 describes the principal characteristics of a typical prilling tower.

Theoretical calculations are possible to determine tower height with reasonable accuracy. Simple parallel streamline flow of both droplets and air is a reasonable assumption in the case of prilling towers compared with the more complex rotational flows produced in spray dryers. For velocity of fall, see, for example, Becker [*Can. J. Chem.,* **37,** 85 (1959)]. For heat transfer, see, for example, Kramers [*Physica,* **12,** 61 (1946)]. Specific design procedures for prilling towers are available in the *Proceedings of the Fertilizer Society (England);* see Berg and Hallie, no. 59, 1960; and Carter and Roberts, no. 110, 1969.

Recent developments in nozzle design have led to drastic reductions in the required height of prilling towers. However, such nozzle designs are largely proprietary and little information is openly available.

TABLE 20-49 Some Characteristics of a Typical Prilling Operation*

Tower size		
Prill tube height, ft	130	
Rectangular cross section, ft	11 by 21.4	
Cooling air		
Rate, lb/h	360,000	
Inlet temperature	Ambient	
Temperature rise, °F	15	
Melt		
		Ammonium nitrate
Type	Urea	
Rate, lb/h	35,200 (190 lb H_2O)	43,720 (90 lb H_2O)
Inlet temperature, °F	275	365
Prills		
Outlet temperature, °F	120	225
Size, mm	Approximately 1 to 3	

*HPD Incorporated. To convert feet to centimeters, multiply by 30.5; to convert pounds per hour to kilograms per hour, multiply by 0.4535; °C = (°F − 32) × 5⁄9.

Flash Drying Special designs of pneumatic-conveyor dryers, described in Sec. 17 can handle filter and centrifuge cakes and other sticky or pasty feeds to yield granular size-enlarged products. The dry product is recycled and mixed with fresh, cohesive feed, followed by disintegration and dispersion of the mixed feed in the drying-air stream.

PRESSURE COMPACTION PROCESSES

The success of compression agglomeration depends on the effective utilization and transmission of the applied external force and on the ability of the material to form and maintain interparticle bonds during pressure compaction (or consolidation) and decompression. Both these aspects are controlled in turn by the geometry of the confined space, the nature of the applied loads and the physical properties of the particulate material and of the confining walls. (See the section on Powder Mechanics and Powder Compaction.)

Pressure compaction is carried out in two classes of equipment. These are **confined-pressure devices** (molding, piston, tableting, and roll presses), in which material is directly consolidated in closed molds or between two opposing surfaces; and **extrusion devices** (pellet mills, screw extruders), in which material undergoes considerable shear and mixing as it is consolidated while being pressed through a die. See Table 20-36 for examples of uses. Product densities and applied pressures are substantially higher than agitative agglomeration techniques, as shown in Fig. 20-71.

Piston and Molding Presses Piston or molding presses are used to create uniform and sometimes intricate compacts, especially in powder metallurgy and plastics forming. Equipment comprises a mechanically or hydraulically operated press and, attached to the platens of the press, a two-part mold consisting of top (male) and bottom (female) portions. The action of pressure and heat on the particulate charge causes it to flow and take the shape of the cavity of the mold. Compacts of metal powders are then sintered to develop metallic properties, whereas compacts of plastics are essentially finished products on discharge from the molding machine.

Tableting Presses Tableting presses are employed in applications having strict specifications for weight, thickness, hardness, density, and appearance in the agglomerated product. They produce simpler shapes at higher production rates than do molding presses. A single-punch press is one that will take one station of tools consisting of an upper punch, a lower punch, and a die. A rotary press employs a rotating round die table with multiple stations of punches and dies. Older rotary machines are single-sided; that is, there is one fill station and one compression station to produce one tablet per station at every revolution of the rotary head. Modern high-speed rotary presses are double-sided; that is, there are two feed and compression stations to

TABLE 20-50 Characteristics of Tableting Presses*

	Single-punch	Rotary
Tablets per minute	8–140	72–6000
Tablet diameter, in.	⅛–4	⅝–2½
Pressure, tons	1½–100	4–100
Horsepower	¼–15	1½–50

*Browning, *Chem. Eng.,* **74**(25), 147 (1967).

NOTE: To convert inches to centimeters, multiply by 2.54; to convert tons to megagrams, multiply by 0.907; and to convert horsepower to kilowatts, multiply by 0.746.

produce two tablets per station at every revolution of the rotary head. Some characteristics of tableting presses are shown in Table 20-50.

For successful tableting, a material must have suitable flow properties to allow it to be fed to the tableting machine. Wet or dry granulation is used to improve the flow properties of materials. In the case of **wet granulation,** agitative granulation techniques such as fluidized beds or mixer granulators as discussed above are often employed.

In **dry granulation,** the blended dry ingredients are first densified in a heavy-duty rotary tableting press which produces "slugs" 1.9 to 2.5 cm (¾ to 1 in) in diameter. These are subsequently crushed into particles of the size required for tableting. Predensification can also be accomplished by using a rotary compactor-granulator system. A third technique, direct compaction, uses sophisticated devices to feed the blended dry ingredients to a high-speed rotary press.

Excellent accounts of tableting in the pharmaceutical industry have been given by Kibbe [*Chem. Eng. Prog.,* **62**(8), 112 (1966)], Carstensen [*Handbook of Powder Science & Technology,* Fayed & Otten (eds.), Van Nostrand Reinhold Inc., **252** (1983)], Stanley-Wood (ed.) (loc. cit.), and Doelker (loc. cit.).

Roll Presses Roll presses compact raw material as it is carried into the gap between two rolls rotating at equal speeds (Fig. 20-90). The size and shape of the agglomerates are determined by the geometry of the roll surfaces. Pockets or indentations in the roll surfaces form briquettes the shape of eggs, pillows, teardrops, or similar forms from a few grams up to 2 kg (5 lb) or more in weight. Smooth or corrugated rolls produce a solid sheet which can be granulated or broken down into the desired particle size on conventional grinding equipment.

Roll presses can produce large quantities of materials at low cost, but the product is less uniform than that from molding or tableting presses. The introduction of the proper quantity of material into each of the rapidly rotating pockets in the rolls is the most difficult problem in the briquetting operation. Various types of feeders have helped to overcome much of this difficulty.

The impacting rolls can be either solid or divided into segments. Segmented rolls are preferred for hot briquetting, as the thermal expansion of the equipment can be controlled more easily.

Roll presses provide a **mechanical advantage** in amplifying the feed pressure P_0 to some maximum value P_m. This maximum pressure

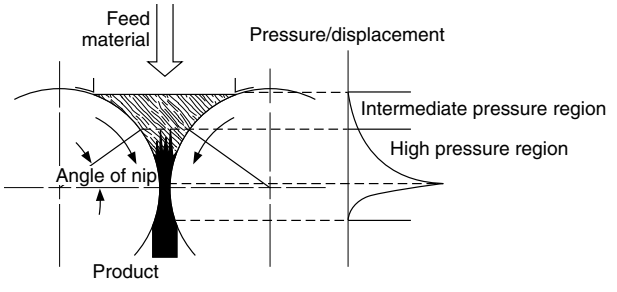


FIG. 20-90 Regions of compression in roll presses. Slippage and particle rearrangement occurs above the angle of nip, and powder compaction at high pressure occurs in the nonslip region below the angle of nip. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries,* Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

P_m and the roll compaction time control compact density. Generally speaking, as compaction time decreases (e.g., by increasing roll speed), the minimum necessary pressure for quality compacts increases. There may be an upper limit of pressure as well for friable materials or elastic materials prone to delamination.

Pressure amplification occurs in two regions of the press (Fig. 20-90). Above the **angle of nip,** sliding occurs between the material and roll surface as material is forced into the rolls, with intermediate pressure ranging from 1–10 psi. Energy is dissipated primarily through overcoming particle friction and cohesion. Below the angle of nip, no slip occurs as the powder is compressed into a compact and pressure may increase up to several thousand psi. Both these intermediate and high-pressure regions of densification are indicated in compressibility diagram of Fig. 20-77.

The overall performance of the press and its mechanical advantage (P_m/P_0) depend on the mechanical and frictional properties of the powder. (See "Powder Mechanics and Powder Compaction" section.) For design procedures, see Johanson [*Proc. Inst. Briquet. Agglom. Bien. Conf.,* **9,** 17 (1965).] Nip angle α generally increases with decreasing compressibility κ, or with increasing roll friction angle ϕ_w and effective angle of friction ϕ_e. Powders which compress easily and have high-friction grip high in the rolls. The mechanical advantage pressure ratio (P_m/P_0) increases and the time of compaction decreases with decreasing nip angle since the pressure is focused over a smaller roll area. In addition, the mechanical advantage generally increases with increasing compressibility and roll friction.

The most important factor that must be determined in a given application is the pressing force required for the production of acceptable compacts. Roll loadings (i.e., roll separating force divided by roll width) in commercial installations vary from 4.4 MN/m to more than 440 MN/m (1000 lb/in to more than 100,000 lb/in). Roll sizes up to 91 cm (36 in) in diameter by 61 cm (24 in) wide are in use.

The roll loading L is related to the maximum developed pressure and roll diameter by

$$L = \frac{F}{W} = \frac{1}{2} f P_m D \propto P_m D^{1/2}(h + d)^{1/2} \qquad (20\text{-}70)$$

where F is the **roll-separating force,** D and W are the roll diameter and width, f is a **roll-force factor** dependent on compressibility κ and gap thickness as given in Fig. 20-91, h is the gap thickness and $d/2$ is the pocket depth for briquette rolls. [Pietsch, *Size Enlargement by Agglomeration,* John Wiley & Sons Ltd., Chichester, 1992.] The maximum pressure P_m is established on the basis of required compact density and quality, and it is a strong function of roll gap distance and powder properties as discussed above, particularly compressibility.

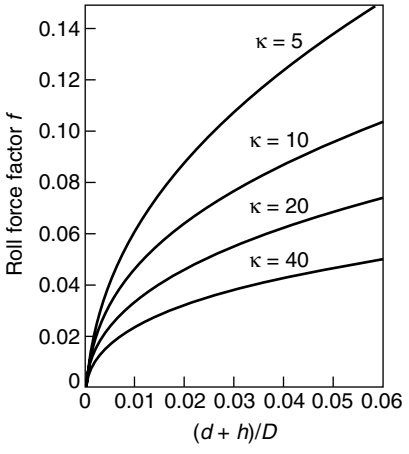


FIG. 20-91 Roll-force factor as a function of compressibility κ and dimensionless gap distance $(d + h)/D$. [*Pietsch (ed.),* Roll Pressing, *Powder Advisory Centre, London (1987).*]

Small variations in feed properties can have a pronounced effect on maximum pressure P_m and press performance. Roll presses are scaled on the basis of constant maximum pressure. The required roll loading increases approximately with the square root of increasing roll diameter or gap width.

The allowable roll width is inversely related to the required pressing force because of mechanical-design considerations. The throughput of a roll press at constant roll speed decreases as pressing force increases since the allowable roll width is less. Machines with capacities up to 45 Mg/h (50 tons/h) are available. Some average figures for the pressing force and energy necessary to compress a number of materials on roll-type briquette machines are given in Table 20-51. Typical capacities are given in Table 20-52.

During compression in the slip region, escaping air may induce fluidization or erratic pulsating of the feed. This effect, which is controlled by the permeability of the powder, limits the allowable roll speed of the press, and may also enduce compact delamination. Increases in roll speed or decreases in permeability require larger feed pressures.

Pellet Mills Pellet mills operate on the principle shown in Fig. 20-92. Moist, plastic feed is pushed through holes in dies of various shapes. The friction of the material in the die holes supplies the resistance necessary for compaction. Adjustable knives shear the rodlike extrudates into pellets of the desired length. Although several designs are in use, the most commonly used pellet mills operate by applying power to the die and rotating it around a freely turning roller with fixed horizontal or vertical axis.

Pellet quality and capacity vary with properties of the feed such as

TABLE 20-51 Pressure and Energy Requirements to Briquette Various Materials*

Pressure range, lb./sq. in.	Approximate energy required, kw.-hr./ton	Type of material being briquetted or compacted		
		Without binder	With binder	Hot
Low 500–20,000	2–4	Mixed fertilizers, phosphate ores, shales, urea	Coal, charcoal, coke, lignite, animal feed, candy	Phosphate ores, urea
Medium 20,000–50,000	4–8	Acrylic resins, plastics, PVC, ammonium chloride, DMT, copper compounds, lead	Ferroalloys, fluorspar, nickel	Iron, potash, glass-making mixtures
High 50,000–80,000	8–16	Aluminum, copper, zinc, vanadium, calcined dolomite, lime, magnesia, magnesium carbonates, sodium chloride, sodium and potassium compounds	Flue dust, natural and reduced iron ores	Flue dust, iron oxide, natural and reduced iron ores, scrap metals
Very high >80,000	>16	Metal powders, titanium	—	Metal chips

*Courtesy Bepex Corporation. To convert pounds per square inch to newtons per square meter, multiply by 6895; to convert kilowatthours per ton to kilowatthours per megagram, multiply by 1.1.

TABLE 20-52 Some Typical Capacities (tons/h) for a Range of Roll Presses*

Roll diameter, in	10	16	12	10.3	13	20.5	28	36
Maximum roll-face width, in	3.25	6	4	6	8	13.5	27	10
Roll-separating force, tons	25	50	40	50	75	150	300	360
Carbon								
Coal, coke		2	1		3	6	25	
Charcoal			8			13		
Activated					3	7		
Metal and ores								
Alumina					5	10	28	
Aluminum				2	4	8	20	
Brass, copper	0.5			1.5	3	6	16	
Steel-mill waste					5	10		
Iron				3	6	15	40	
Nickel powder					2.5	5.0		
Nickel ore						20	40	
Stainless steel				2	5	10		
Steel								25
Bauxite		1.5				10	20	
Ferrometals						10		
Chemicals								
Copper sulfate	0.5	1.5		1	3	6	15	
Potassium hydroxide				1	4	8		
Soda ash	0.5				3	6	15	
Urea	0.25					10		
DMT	0.25				2	6		
Minerals								
Potash						20	80	
Salt				2	5	9		
Lime					4	8	15	
Calcium sulfate							13	40
Fluorspar						5	10	28
Magnesium oxide						1.5	5	
Asbestos						1.5	3	
Cement						5		
Glass batch						5	12	

*Courtesy Bepex Corporation. To convert inches to centimeters, multiply by 2.54; to convert tons to megagrams, multiply by 0.907; and to convert tons per hour to megagrams per hour, multiply by 0.907.

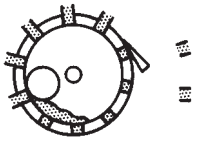


FIG. 20-92 Operating principle of a pellet mill.

moisture, lubricating characteristics, particle size, and abrasiveness, as well as die characteristics and speed. A readily pelleted material will yield about 122 kg/kWh [200 lb/(hp·h)] by using a die with 0.6-cm (¼-in) holes. Some characteristics of pellet mills are given in Table 20-53.

Screw Extruders Screw extruders employ a screw to force material in a plastic state continuously through a die. If the die hole is round, a compact in the form of a rod is formed, whereas if the hole is a thin slit, a film or sheet is formed. Many other forms are also possible.

Basic types of extruders include axial end plate, radial screen, rotary cylinder or gear, and ram or piston. For a review, see Newton [*Powder Technology & Pharmaceutical Processes,* Chulia et al. (eds.), Elsevier, 391 (1994).]

Both wet and dry extrusion techniques are available, and both are strongly influenced by the frictional properties of the particulate phase and wall. In the case of wet extrusion, rheological properties of the liquid phase are equally important. See Pietsch [*Size Enlargement by Agglomeration,* John Wiley & Sons Ltd., Chichester, 346 (1992)] and Benbow et al. [*Chem. Eng. Sci.,* **422,** 2151 (1987)] for a review of design procedures for dry and wet extrusion, respectively.

A common use of screw extruders is in the forming and compounding of plastics. Table 20-54 shows typical outputs that can be expected per horsepower for various plastics and the characteristics of several popular extruder sizes.

Deairing pug-mill extruders which combine mixing, densification, and extrusion in one operation are available for agglomerating clays, catalysts, fertilizers, etc. Table 20-55 gives data on screw extruders for the production of catalyst pellets.

THERMAL PROCESSES

Bonding and agglomeration by temperature elevation or reduction are applied either in conjunction with other size-enlargement processes or as a separate process. Agglomeration occurs through one or more of the following mechanisms:

1. Drying of a concentrated slurry or wet mass of fines
2. Fusion
3. High-temperature chemical reaction
4. Solidification and/or crystallization of a melt or concentrated slurry during cooling

Sintering and Heat Hardening In powder metallurgy compacts are sintered with or without the addition of binders. In ore processing the agglomerated mixture is either sintered or indurated. Sintering refers to a process in which fuel is mixed with the ore and burned on a grate. The product is a porous cake. Induration, or heat hardening, is accomplished by combustion of gases passed through the bed. The aim is to harden the pellets without fusing them together, as is done in the sintering process.

Ceramic bond formation and grain growth by diffusion are the two prominent reactions for bonding at the high temperature (1100 to 1370°C, or 2000 to 2500°F, for iron ore) employed. The minimum temperature required for sintering may be measured by modern **dilatometry** techniques, as well as by differential scanning calorimetry. See Compo et al. [*Powder Tech.,* **51**(1), 87 (1987); *Particle Characterization,* **1,** 171 (1984)] for reviews.

In addition to agglomeration, other useful processes may occur during sintering and heat hardening. For example, carbonates and sulfates may be decomposed, or sulfur may be eliminated. Although the major application is in ore beneficiation, other applications, such as the preparation of lightweight aggregate from fly ash and the formation of clinker from cement raw meal, are also possible. Nonferrous sinter is produced from oxides and sulfides of manganese, zinc, lead, and nickel. An excellent account of the many possible applications is given by Ban et al. [Knepper (ed.), *Agglomeration,* op. cit. p. 511] and Ball et al. [Agglomeration of Iron Ores (1973)]. The highest tonnage use at present is in the beneficiation of iron ore.

The machine most commonly used for sintering iron ores is a traveling grate, which is a modification of the Dwight-Lloyd continuous sintering machine formerly used only in the lead and zinc industries. Modern sintering machines may be 4 m (13 ft) wide by 60 m (200 ft) long and have capacities of 7200 Mg/day (8000 tons/day).

TABLE 20-53 Characteristics of Pellet Mills

Horsepower range	10–250
Capacity, lb/(hp·h)	75–300
Die characteristics	
Size	Up to 26 in inside diameter × approximately 8 in wide
Speed range	75-500 r/min
Hole-size range	1/16–1¼ in inside diameter
Rollers	As many as three rolls; up to 10-in diameter

NOTE: To convert horsepower to kilowatts, multiply by 0.746; to convert pounds per horsepower-hour to kilograms per kilowatthour, multiply by 0.6; and to convert inches to centimeters, multiply by 2.54.

TABLE 20-54 Characteristics of Plastics Extruders*

Efficiencies	lb/(hp·h)
Rigid PVC	7–10
Plasticized PVC	10–13
Impact polystyrene	8–12
ABS polymers	5–9
Low-density polyethylene	7–10
High-density polyethylene	4–8
Polypropylene	5–10
Nylon	8–12

Relation of size, power, and output

	Diameter		
hp	in	mm	Output, lb/h, low-density polyethylene
15	2	45	Up to 125
25	2½	60	Up to 250
50	3½	90	Up to 450
100	4½	120	Up to 800

**The Encyclopedia of Plastics Equipment,* Simonds (ed.), Reinhold, New York, 1964.

NOTE: To convert inches to centimeters, multiply by 2.54; to convert horsepower to kilowatts, multiply by 0.746; to convert pounds per hour to kilograms per hour, multiply by 0.4535; and to convert pounds per horsepower-hour to kilograms per kilowatthour, multiply by 0.6.

TABLE 20-55 Characteristics of Pelletizing Screw Extruders for Catalysts*

Screw diameter, in	Drive hp	Typical capacity, lb/h
2.25		60
4	7.5–15	200–600
6	Up to 60	600–1500
8	75–100	Up to 2000

*Courtesy The Bonnot Co. To convert inches to centimeters, multiply by 2.54; to convert horsepower to kilowatts, multiply by 0.746; and to convert pounds per hour to kilograms per hour, multiply by 0.4535.

NOTE:

1. Typical feeds are high alumina, kaolin carriers, molecular sieves, and gels.
2. Water-cooled worm and barrel, variable-speed drive.
3. Die orifices as small as 1/16 in.
4. Vacuum-deairing option available.

The productive capacity of a sintering strand is related directly to the rate at which the burning zone moves downward through the bed. This rate, which is of the order of 2.5 cm/min (1 in/min), is controlled by the air rate through the bed, with the air functioning as the heat-transfer medium.

Heat hardening of green iron-ore pellets is accomplished in a vertical shaft furnace, a traveling-grate machine, or a grate-plus-kiln combination (see Ball et al., op. cit.).

Drying and Solidification Granular free-flowing solid products are often an important result of the drying of concentrated slurries and pastes and the cooling of melts. Size enlargement of originally finely divided solids results. Pressure agglomeration including extrusion, pelleting, and briquetting is used to preform wet material into forms suitable for drying in through-circulation and other types of dryers. Details are given in Sec. 12 in the account of solids-drying equipment.

Rotating-drum-type and belt-type heat-transfer equipment forms granular products directly from fluid pastes and melts without intermediate preforms. These processes are described in Sec. 5 as examples of indirect heat transfer to and from the solid phase. When solidification results from melt freezing, the operation is known as *flaking.* If evaporation occurs, solidification is by drying.

MODELING AND SIMULATION OF GRANULATION PROCESSES

For granulation processes, granule size distribution is an important if not the most important property. The evolution of the granule size distribution within the process can be followed using population balance modeling techniques. This approach is also used for other size-change processes including crushing and grinding (Sec. 20: "Principles of Size Reduction") and crystallization (Sec. 18). The use of the **population balance (PB)** is outlined briefly below. For more in-depth analysis see Randolph & Larson (*Theory of Particulate Processes, 2d ed.,* Academic Press, 1991), Ennis & Litster (*The Science and Engineering of Granulation Processes,* Chapman-Hall, 1997), and Sastry & Loftus [*Proc. 5th Int. Symp. Agglom.,* IChemE, 623 (1989)].

The key uses of PB modeling of granulation processes are:

- Critical evaluation of data to determine controlling granulation mechanisms
- In design, to predict the mean size and size distribution of product granules
- Sensitivity analysis: to analyze quantitatively the effect of changes to operating conditions and feed variables on product quality
- Circuit simulation, optimization, and process control

The use of PB modeling by practitioners has been limited for two reasons. First, in many cases the kinetic parameters for the models have been difficult to predict and are very sensitive to operating conditions. Second, the PB equations are complex and difficult to solve. However, recent advances in understanding of granulation micromechanics, as well as better numerical solution techniques and faster computers, means that the use of PB models by practitioners should expand.

THE POPULATION BALANCE

The PB is a statement of continuity for particulate systems. It includes a **kinetic expression** for each mechanism which changes a particle property. Consider a section of a granulator as illustrated in Fig. 20-93. The PB follows the change in the granule size distribution as granules are born, die, grow, and enter or leave the control volume. As discussed in detail previously ("Agglomeration Rate Processes"), the granulation mechanisms which cause these changes are nucleation, layering, coalescence, and attrition (Tables 20-39 and 20-56). The number of particles-per-unit volume of granulator between size volume v and $v + dv$ is $n(v)dv$, where $n(v)$ is the **number frequency size distribution** by size volume, having dimensions of number per-unit-granulator and volume per-unit-size volume. For constant granulator volume, the macroscopic PB for the granulator in terms of $n(v)$ is:

$$\frac{\partial n(v,t)}{\partial t} = \frac{Q_{in}}{V} n_{in}(v) - \frac{Q_{ex}}{V} n_{ex}(v) - \frac{\partial (G^* - A^*) n(v,t)}{\partial v} + B_{nuc}(v) + \frac{1}{2N_t} \int_0^v \beta(u, v-u, t) n(u,t) n(v-u,t) du - \frac{1}{N_t} \int_0^\infty \beta(u,v,t) n(u,t) n(v,t) du \quad (20\text{-}71)$$

where V is the volume of the granulator; Q_{in} and Q_{ex} are the inlet and exit flow rates from the granulator; $G(v)$, $A(v)$, and $B_{nuc}(v)$ are the layering, attrition, and nucleation rates, respectively; $\beta(u,v,t)$ is the coalescence kernel and N_t is the total number of granules-per-unit volume of granulator. The left-hand side of Eq. 20-71 is the accumulation of particles of a given size volume. The terms on the right-hand side are in turn: the bulk flow into and out of the control volume, the convective flux along the size axis due to layering and attrition, the birth of new particles due to nucleation, and birth and death of granules due to coalescence. Equation 20-71 is written in terms of granule volume v, but could also be written in terms of granule size x or could also be expanded to follow changes in other granule properties, e.g., changes in granule density or porosity due to consolidation.

MODELING INDIVIDUAL GROWTH MECHANISMS

The **granule size distribution (GSD)** is a strong function of the balance between different mechanisms for size change shown in Table 20-53—layering, attrition, nucleation, and coalescence. For example, Fig. 20-94 shows the difference in the GSD for a doubling in mean granule size due to (1) layering only, or (2) coalescence only for batch, plug-flow, and well-mixed granulators. Table 20-56 describes how four key rate mechanisms effect the GSD.

Nucleation Nucleation increases both the mass and number of the granules. For the case where new granules are produced by liquid

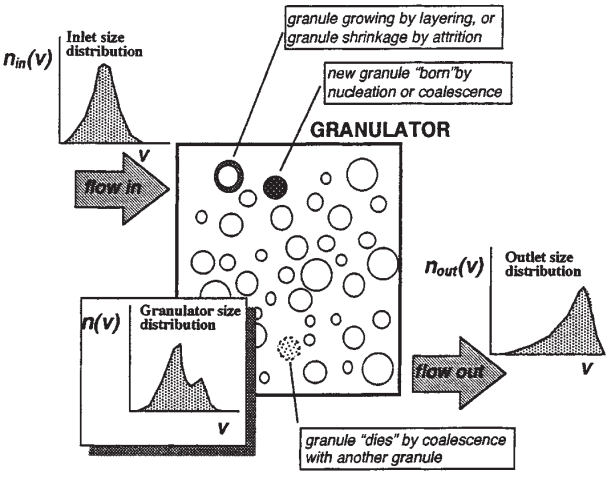


FIG. 20-93 Changes to the granule size distribution due to granulation-rate processes as particles move through the granulator. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries,* Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

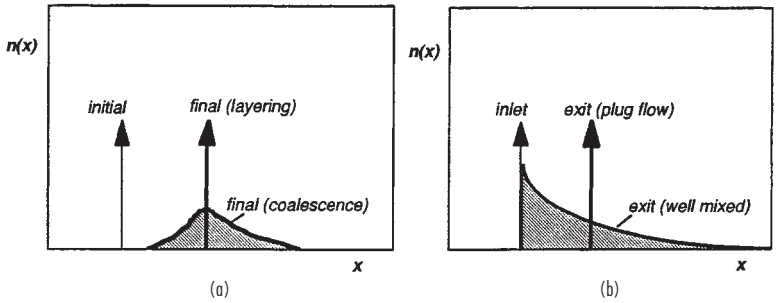


FIG. 20-94 The effect of growth mechanism and mixing on product granule size distribution for (*a*) batch growth by layering or coalescence, and (*b*) layered growth in well-mixed or plug-flow granulators. Reprinted from *Granulation and Coating Technologies for High-Value-Added Industries,* Ennis and Litster (1996) with permission of E & G Associates. All rights reserved.

feed which dries or solidifies, the nucleation rate is given by the new feed droplet size n_s and the volumetric spray rate S:

$$B(v)_{\text{nuc}} = Sn_S(v) \tag{20-72}$$

In processes where new powder feed has a much smaller particle size than the smallest granular product, the feed powder can be considered as a **continuous phase** which can nucleate to form new granules [Sastry & Fuerstenau, *Powder Tech.,* **7,** 97 (1975)]. The size of the nuclei is then related to nucleation mechanism. In the case of nucleation by spray, the size of the nuclei is of the order of the droplet size and proportional to cosθ, where θ is binder fluid-particle contact angle (see Fig. 20-67 of "Wetting" section).

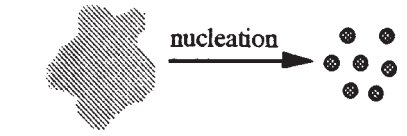
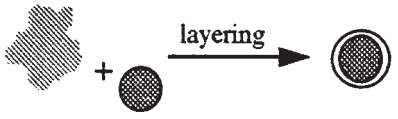
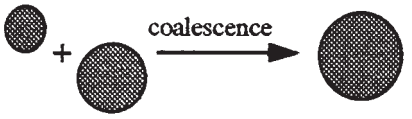
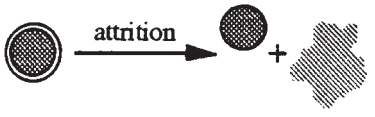
Layering Layering increases granule size and mass by the progressive coating of new material onto existing granules, but it does not alter the number of granules in the system. As with nucleation, the new feed may be in liquid form (where there is simultaneous drying or cooling) or may be present as a fine powder. Where the feed is a powder, the process is sometimes called **pseudolayering** or **snowballing.** It is often reasonable to assume a linear-growth rate $G(x)$ which is independent of granule size. For batch and plug-flow granulators, this causes the initial feed distribution to shift forward in time with the shape of the GSD remaining unaltered and governed by a traveling-wave equation (Table 20-59). As an example, Fig. 20-95 illustrates size-independent growth of limestone pellets by snowballing in a batch drum. Size-independent linear growth rate implies that the volumetric growth rate $G^*(v)$ is proportional to projected granule surface area, or $G^*(v) \propto v^{2/3} \propto x^2$. This assumption is true only if all granules receive the same exposure to new feed. Any form of segregation will invalidate this assumption [Liu and Litster, *Powder Tech.,* **74,** 259 (1993)]. The growth rate $G^*(v)$ by layering only can be calculated directly from the mass balance:

$$\dot{V}_{\text{feed}} = (1 - \varepsilon) \int_0^\infty G^*(v)n(v)dv \tag{20-73}$$

where $\dot{V}_{\text{feed}}$ is the volumetric flow rate of new feed and ε is the granule porosity.

Coalescence Coalescence is the most difficult mechanism to model. It is easiest to write the population balance (Eq. 20-71) in terms of number distribution by volume $n(v)$ because granule volume is conserved in a coalescence event. The key parameter is the **coalescence kernel** or rate constant $\beta(u,v)$. The kernel dictates the overall rate of coalescence, as well as the effect of granule size on coalescence

TABLE 20-56 Impact of Granulation Mechanisms on Size Distribution

Mechanism	Changes number of granules?	Changes mass of granules?	Discrete or differential?
	yes	yes	discrete
	no	yes	differential
	yes	no	discrete
	no	yes	differential

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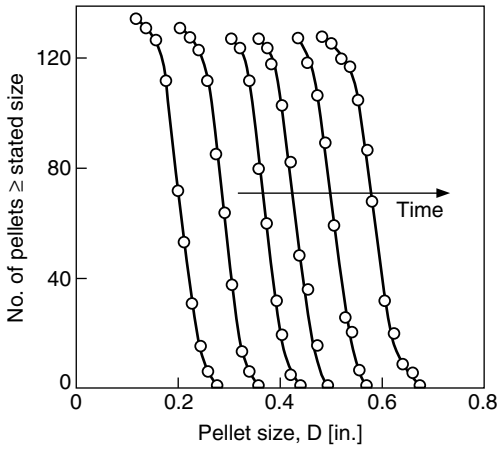


FIG. 20-95 Batch drum growth of limestone pellets by layering with a size-independent linear growth rate [*Capes,* Chem. Eng., ***45,*** *CE78 (1967).*]

rate. The **order** of the kernel has a major effect on the shape and evolution of the granule size distribution. [See Adetayo & Ennis, *AIChE J.* 1997 (In press).] Several empirical kernels have been proposed and used (Table 20-57).

All the kernels are empirical, or semiempirical and must be fitted to plant or laboratory data. The kernel proposed by Adetayo and Ennis is consistent with the granulation regime analysis described above (see section on growth) and is therefore recommended:

$$\beta(u,v) = \begin{cases} k, w < w^* \\ 0, w > w^* \end{cases} \quad w = \frac{(uv)^a}{(u+v)^b} \tag{20-74}$$

where w^* is the **critical average granule volume** in a collision corresponding to $St = St^*$, and it is related to the critical cutoff diameter defined above (Eq. 20-47). For fine powders in the noninertial regime (See section on growth) where $St << St^*$, this kernel collapses to the simple **random** or size-independent kernel $\beta = k$ for which the mean granule size increases exponentially with time (Eq. 20-51). Where deformation is unimportant, coalescence occurs only in the noninertial regime and stops abruptly when $St_v = St_v^*$. Based on the granulation regime analysis, the effects of feed characteristics and operating variables on granulation extent has been predicted [Adetayo et al., *Powder Tech.,* **82,** 47–59 (1995)]. (See "Extent of Noninertial Growth" subsection.)

Modeling growth where deformation is significant is more difficult. It can be assumed that a critical cutoff size exists w^* which determines which combination of granule sizes are capable of coalescence, based on their inertia. When the harmonic average of sizes of two colliding granules w is less than this critical cut-off size w^*, coalescence is successful, or

$$w = \frac{(uv)^b}{(u+v)^a} = w^* = \frac{\pi}{6}\left(\frac{16\mu}{\rho u_0} St^*\right)^3 \tag{20-75}$$

where a and b are model parameters expected to vary with granule deformability, and u and v are granule volumes. To be dimensionally consistent, $2b - a = 1$. w^* and w involving the parameters a and b represent a generalization of the Stokes analysis for non-deforming systems, for which case $a = b = 1$. For deformable systems, the kernel is then represented by Eq. 20-74. Figure 20-96 illustrates the evolution of the granule size distribution as predicted by this cutoff-based kernel which accounts for deformability. The cutoff kernel is seen to clearly track the experimental average granule size over the life of the granulation, illustrating that multiple kernels are not necessary to describe the various stages of granule growth, including the initial stage of random noninertial coalescence and the final stage of nonrandom preferential inertial growth by balling or crushing and layering (see Table 20-39).

Attrition The wearing away of granule surface material by attrition is the direct opposite of layering. It is an important mechanism when drying occurs simultaneously with granulation and granule velocities are high, e.g., fluidized beds and spouted beds. In a fluid bed [Ennis & Sunshine, *Tribology International,* **26,** 319 (1993)], attrition rate is proportional to excess gas velocity $(U - U_{mf})$ and approximately inversely proportional to granule-fracture toughness K_c, or $A \propto (U - U_{mf})/K_c$. For spouted beds, most attrition occurs in the spout and the attrition rate may be expressed as:

$$A \propto \frac{A_i U_i^3}{K_c} \tag{20-76}$$

where A_i and U_i are the inlet orifice area and gas velocity, respectively. Attrition rate also increases with increasing slurry feed rate [Liu and Litster, *Powder Tech.,* **74,** 259 (1993)]. Granule breakage by fragmentation is also possible, with its rate being described by an **on function** which plays a similar role as the coalescence kernel does for growth. (See "Principles of Size Reduction" and "Breakage" sections for additional details.)

SOLUTION OF THE POPULATION BALANCE

Effects of Mixing As with chemical reactors, the **degree of mixing** within the granulator has an important effect on the final granule size distribution because of its influence on the **residence time distribution.** Fig. 20-94 shows the difference in exit size distribution for a plug-flow and well-mixed granulator for growth by layering only. In general, the exit size distribution is broadened and the extent of growth (for constant rate constants) is diminished for an increased degree of mixing in the granulator. With layering and attrition rates playing the role of generalized velocities, coalescence, and fragmentation rates, the role of reaction rate constants, methodologies of traditional reaction engineering may be employed to design granu-

TABLE 20-57 Coalescence Kernels for Granulation

Kernel	Reference and comments
$\beta = \beta_o$	Kapur & Fuerstenau [*I&EC Proc. Des. & Dev.,* **8**(1), 56 (1969)], size-independent kernel.
$\beta = \beta_o \frac{(u+v)^a}{(uv)^b}$	Kapur [*Chem. Eng. Sci.,* **27,** 1863 (1972)], preferential coalescence of limestone.
$\beta = \beta_o \frac{(u^{2/3}+v^{2/3})}{1/u+1/v}$	Sastry [*Int. J. Min. Proc.,* **2,** 187 (1975)], preferential balling of iron ore and limestone.
$\beta(u,v) = \begin{cases} k, & w < w^* \\ 0, & w > w^* \end{cases} \quad w = \frac{(uv)^a}{(u+v)^b}$	Adetayo & Ennis [*AIChE J.,* (1997) In press], based on granulation regime analysis.

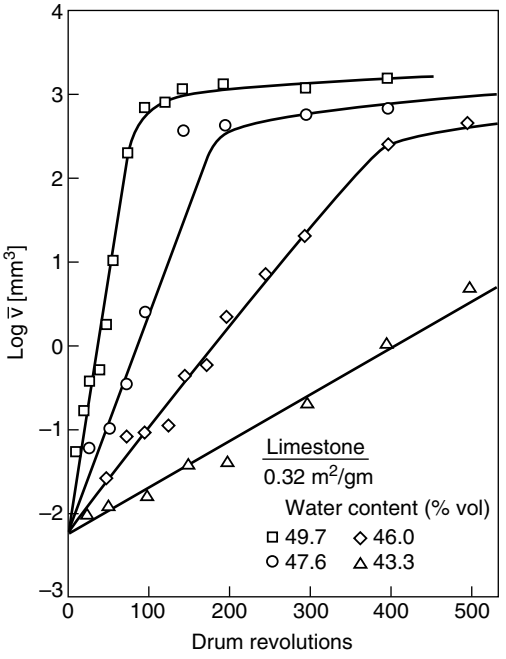


FIG. 20-96 Batch drum growth of limestone by coalescence. Note granule size increases exponentially with time in the first stage of noninertial growth. Experimental data of Kapur [Adv. Chem. Eng., ***10,*** *56 (1978)*] compared with single deformable granulation kernel (Eqs. 20-74, 20-75). [*Adetayo & Ennis,* AIChEJ. *(*In press).] Reproduced with permission of the American Institute of Chemical Engineers. Copyright AIChE. All rights reserved.

lation systems or optimize the granule size distribution. [For the related example of crystallization, see Randolph & Larson (*Theory of Particulate Processes,* 2d ed., Academic Press, 1991).] Table 20-58 lists some mixing models that have been used for several types of granulators.

Analytical Solutions Solution of the population balance is not trivial. Analytical solutions are available for only a limited number of special cases, of which some of examples of practical importance are summarized in Table 20-59. For other analytical solutions, see general references on population balances given above.

In general, analytical solutions are only available for specific initial or inlet size distributions. However, for batch granulation where the only growth mechanism is coalescence, at long times the size distribution may become **self-preserving.** The size distribution is self-preserving if the normalized size distributions $\varphi = \varphi(\eta)$ at long time are independent of mean size $\bar{v}$, or

$$\varphi = \varphi(\eta) \quad \text{only where} \quad \eta = v/\bar{v}$$

$$\bar{v} = \int_0^\infty v \cdot n(v,t)\, dv \tag{20-77}$$

Analytical solutions for self-preserving growth do exist for some coalescence kernels and such behavior is sometimes seen in practice (Fig. 20-97). Roughly speaking, self-preserving growth implies that the width of the size distribution increases in proportion to mean granule size, i.e., the width is uniquely related to the mean of the distribution.

Numerical Solutions For many practical applications, numerical solutions to the population balance are necessary. Several numerical solution techniques have been proposed. It is usual to break the size range into discrete intervals and then solve the resulting series of ordinary differential equations. A geometric discretization reduces the number of size intervals (and equations) that are required. Litster et al. [*AIChE J.,* (1995)] give a general discretized PB for nucleation, growth, and coalescence with a geometric discretization of $v_j = 2^{1/q} v_{j-1}$ where q is an integer. Accuracy is increased (at the expense of

TABLE 20-58 Mixing Models for Continuous Granulators

Granulator	Mixing Model	Reference
Fluid bed	Well-mixed	See Sec. 17
Spouted bed	Well-mixed	Liu and Litster, *Powder Tech.,* **74,** 259 (1993)
	Two-zone model	Litster, et al. [*Proc. 6th Int. Symp. Agglom., Soc. Powder Tech., Japan,* **123** (1993).
Drum	Plug-flow	Adetayo et al., *Powder Tech.,* **82,** 47–59 (1995)
Disc	Two well-mixed tanks in series with classified exit	Sastry & Loftus [*Proc. 5th Int. Symp. Agglom.,* IChemE, 623 (1989)]
	Well-mixed tank and plug-flow in series with fines bypass	Ennis, Personal communication (1986)

TABLE 20-59 Some Analytical Solutions to the Population Balance*

Mixing state	Mechanisms operating	Initial or inlet size distribution	Final or exit size distribution
Batch	Layering only: $G(x) = constant$	Any initial size distribution, $n_0(x)$	$n(x) = n_0(x - \Delta x)$ *where* $\Delta x = Gt$
Continuous & well-mixed	Layering only: $G(x) = constant$	$n_{in}(x) = N_{in}\,\delta(x - x_{in})$	$n(x) = \dfrac{N_0 G}{\tau} \exp\left(-\dfrac{\tau(x - x_{in})}{G}\right)$
Batch	Coalescence only, size independent:	$n_o(v) = N_0 \delta(v - v_o)$	$n(v) = \dfrac{N_0}{\bar{v}} \exp\left(-\dfrac{v}{\bar{v}}\right)$
	$\beta(u, v) = \beta_o$		*where* $\bar{v} = v_0 \exp\left(\dfrac{\beta_o t}{6}\right)$
Batch	Coalescence only, size independent: $\beta(u, v) = \beta_o$	$n_o(v) = \dfrac{N_0}{v_0} \exp\left(-\dfrac{v}{v_o}\right)$	$n(v) = \dfrac{4\,N_0}{v_0(N_0\beta_o t + 2)^2} \exp\left[\dfrac{-2v/v_0}{N_0\beta_o t + 2}\right]$

*Randolph and Larson, *Theory of Particulate Processes,* 2d ed., Academic Press, New York (1988); Gelbart and Seinfeld, *J. Computational Physics,* **28,** 357 (1978).

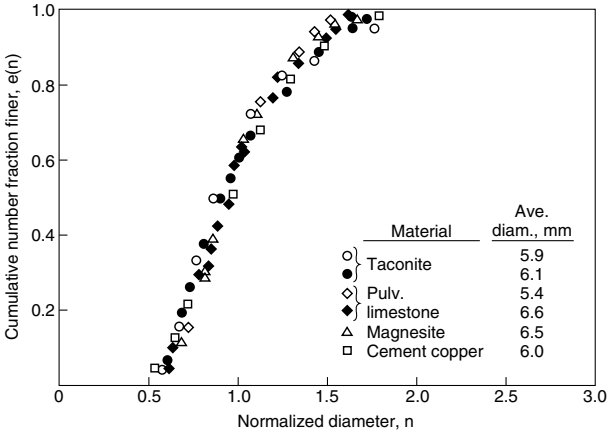


FIG. 20-97 Self-preserving size distributions for batch coalescence in drum granulation. [*Sastry,* Int. J. Min. Proc., **2,** *187 (1975).*] With kind permission of Elsevier Science -NL, 1055 KV Amsterdam, the Netherlands.

computational time) by increasing the value of q. Their discretized PB is recommended for general use.

SIMULATION OF GRANULATION CIRCUITS WITH RECYCLE

When granulation circuits include recycle streams, both steady-state and dynamic responses can be important. Computer simulation packages are now widely used to design and optimize many process flow sheets, e.g., comminution circuits, but simulation of granulation circuits is much less common. Commercial packages do not contain library models for granulators. Some researchers have developed simulations and used these for optimization and control studies [Sastry, *Proc. 3rd Int. Symp. Agglom.* (1981); Adetayo et al., *Computers Chem. Eng.*, **19,** 383 (1995); Zhang et al., *Control of Part. Processes IV* (1995)]. For these simulations, dynamic population-balance models have been used for the granulator. Standard literature models are used for auxiliary equipment such as screens, dryers, and crushers. These simulations are valuable tools for optimization studies and development of control strategies in granulation circuits, and may be employed to investigate the effects of transient upsets in operating variables, particularly moisture level and recycle ratio, on circuit performance.

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Handling of Bulk Solids and Packaging of Solids and Liquids

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INTRODUCTION

During the period between this edition and the sixth, notable changes have taken place which influence packaging and material handling in the chemical industry. These are: Rapid change in the technologies involved; the impact of governmental regulations on both packages and equipment; and the global nature of the chemical industry. These are all interrelated and must be taken into account by the chemical engineer who is planning and choosing packages for chemical products and the packaging machinery and material handling equipment which will be used. Packaging and material handling technology—which had largely been an art, blending science and engineering—has seen dramatic changes. Influencing these are: The advent of special purpose and personal computers; availability of software which allows the rapid calculation and presentation of data and control of processes; and the unusual degree of development of sensing devices.

With these technologies, literally anything in the operation of a packaging or material handling system can be sensed and then via computer, using most often commercially available software, incredible levels of calculations can be performed. These can be used to control the process producing the data and can present operators, engineers, and managers with data and calculations describing virtually any facet of the packaging or material handling systems operation. Closely akin to these is the advent of robots which can carry out many human tasks. Robots are controlled by computers, under the direction of software which relies on sensors and computers. A further outgrowth of this technical revolution occurs in the management and control of inventories—whether they be in the raw material stage, in processing, or in a finished goods sales warehouse. Automatic storage and retrieval equipment under the direction of a special-purpose computer allows unbelievable degrees of identifying all items in the inventory: Where they are, their age, and which inventory to choose to optimize the profit plan of the corporation which owns them. Underlying the control of this sophisticated inventory-management system is an emerging technology known as **bar coding.** This is a logical outgrowth of the development of the personal computer and the software for its operation. The placing of lasers into printing devices has created the ability to produce labels with bar codes. Production of labels has become a real-time packaging-line-type operation rather than an operation in which the labels have to be ordered and inventoried, as was the case before the dramatic technical revolution just described.

The weighing and proportioning of liquids and solids has also benefited from this technical revolution. Sensing devices and special-purpose computers give a level of precision and speed not possible in the era of electromechanical devices. The net result is that packaging and material handling systems now have the sophistication of chemical processes.

All of this gives the chemical engineer new levels of ability to design, operate, and manage complex material handling and packaging systems. Since it is still incumbent on the engineer to define production and performance requirements, some definitions of productivity are useful.

PHYSICAL-DISTRIBUTION CONCEPT

Systems Approach **Physical distribution** is a term applied to a systems concept that comprises the entire spectrum of materials movement. The system begins with the storage and handling of raw materials and follows right on through the packaging and disposition of the finished product. The aim is the attainment of the **lowest overall cost** for the system as a whole, comprising the expenses borne by the manufacturer, transport carrier, warehouser, distributor, and customer. Even the manner in which the customer will handle the product is often taken into account.

Two main benefits accrue from a systems approach to materials handling and packaging. First, a trade-off of investment and operating costs is made possible; higher costs in some parts of a system become permissible in return for much lower costs in other parts. The net result is usually the lowest overall cost. If this is not the case, the reasons for incurring the higher costs can be identified and justified. The second benefit is that customers are not offended by ill-conceived packages, delivery vehicles, or product characteristics.

Mathematical modeling, using digital computers, aids in performing a systems-type analysis for either the entire system or parts of it. By means of integer or linear-programming techniques, optimum systems can be identified. The dynamic performance of these can then be determined by simulation techniques.

Determining the capacities of material-handling and packaging equipment is a primary consideration. Many **interacting variables** often are involved, such as an ever-changing or intermittent material-delivery rate, the capacity of intermediate storage and receiver bins, random stoppage or failure of equipment in the system, and the setup and cleanup time between product grades or blends. Variables frequently interact in such complex ways that conventional capacity analyses are impossible, especially if the interaction varies with time. Under such conditions the question of whether the system will deliver the required output can be answered only by simulation techniques.

Even when a total system analysis is unnecessary, the methodology of mathematical modeling is useful, because by considering each component of a system as a block of a flow sheet, the interrelationships become much clearer. Additional alternatives often become apparent, as does the need for more equipment-performance data.

Capacity Definitions In any analysis, the capacity per unit time of dynamic equipment (such as conveyors and bagging machines), as well as the rates at which they actually perform, must be defined more precisely and realistically than by a mere statement of kilograms or pounds per hour. Some useful definitions employed by the equipment industry are the following:

Instantaneous Rate This is a short-term rate when the equipment operates at the design rate or faster. Typical is the average weight handled over a short period of time, not exceeding 5 min.

Hourly Rate This intermediate rate takes into account equipment stoppages due principally to mechanical downtime rather than the equipment's idle time while it waits for action by other parts of the system.

Shift Rate A long-term rate, this reflects all causes of downtime, including idle time. Thus, the average per shift will vary, but by examining its range the practical capacity can be determined. Production time lost due to scheduling of the equipment affects the shift rate. On certain days the equipment has a shift rate close to the hourly rate, while on other days this rate is only half of the hourly rate. Examination of the reasons for this difference often identifies scheduled events as being responsible: the equipment was shut down for cleanup between product grades, product was unavailable for packaging because a bulk order had to be filled, or the product scheduled had a production rate which was half of the products normally made.

These capacity definitions are used to define responsibilities of both vendors and buyers. For instance, often a vendor is called in to

examine a piece of equipment that does not perform at the "guaranteed" rate. Records of shift production are offered as proof. Yet the vendor then makes a test and shows that the guaranteed rate is met over a short interval. Who is correct? By defining rates the engineer responsible for the installation not only can avoid these situations but can obtain a better appreciation of potential plant situations.

CONVEYING OF BULK SOLIDS

CONVEYOR SELECTION

Selection of the correct conveyor for a specific bulk material in a specific situation is complicated by the large number of interrelated factors that must be considered. First, the alternatives among basic types must be weighed, and then the correct model and size must be chosen. Workability is the first criterion, but the degree of performance perfection that can be afforded must be established.

Because **standardized equipment designs** and complete engineering data are available for many common types of conveyors, their performance can be accurately predicted when they are used with materials having well-known conveying characteristics. However, even the best conveyors can perform disappointingly if material characteristics are unfavorable. It is often true that conveyor engineering is more of an art than a science; problems involving unusual materials or equipment should be approached with caution.

Many preengineered conveyor components can be purchased off the shelf; they are economical and easy to assemble, and they perform well on conventional applications (for which they are designed). However, it is advisable to check with the manufacturer to be sure that the application is proper.

Capacity requirement is a prime factor in conveyor selection. Belt conveyors, which can be manufactured in relatively large sizes to operate at high speeds, deliver large tonnages economically. On the other hand, screw conveyors become extremely cumbersome as they get larger and cannot be operated at high speeds without creating serious abrasion problems.

Length of travel is definitely limited for certain types of conveyors. With high-tensile-strength belting, the length limit on belt conveyors can be a matter of miles. Air conveyors are limited to 305 m (1000 ft); vibrating conveyors, to hundreds of meters or feet. In general, as length of travel increases, the choice among alternatives becomes narrower.

Lift can usually be handled most economically by vertical or inclined bucket elevators, but when lift and horizontal travel are combined, other conveyors should be considered. Conveyors that combine several directions of travel in a single unit are generally more expensive, but since they require only a single drive, this feature often compensates for the added base cost.

Material characteristics, both chemical and physical, should be considered, especially flowability. Abrasiveness, friability, and lump size are also important. Chemical effects (e.g., the effect of oil on rubber or of acids on metal) may dictate the structural materials out of which conveyor components are fabricated. Moisture or oxidation effects from exposure to the atmosphere may be harmful to the material being conveyed and require total enclosure of the conveyor or even an artificial atmosphere. Obviously, certain types of conveyors lend themselves to such special requirements better than others.

Processing requirements can be met by some conveyors with little or no change in design. For example, a continuous-flow conveyor may provide a desired cooling of the solids simply because it puts the conveyed material into direct contact with heat-conducting metals. Screen decks can be readily attached to vibrating conveyors for simple sizing and scalping operations, and special flights or casings on screw conveyors are available for a wide variety of processing operations such as mixing, dewatering, heating, and cooling.

Initial cost of a conveyor system is usually related to **life expectancy** as well as to the flow rate chosen. There is a great temptation to overdesign, which should be resisted. The first really long-distance belt conveyor was designed and fabricated to extremely high standards of quality. After 35 years it was still in operation with almost all its original components. Had this operation been planned for only a 10-year life, the conveyor system would have represented a bad case of overdesign. While there is a market for used conveyor equipment, it is extremely limited. Thus, it is important to choose conveyor quality for expected life of project.

Comparative costs for conveyor systems can be based only on studies of specific problems. For example, belt-conveyor idlers are available in a range of qualities that may make the best unit cost three times as much as the cheapest. Bearing quality, steel thickness, and diameter of rolls all affect cost, as does design for easy maintenance and repair. Therefore, it is necessary to make cost comparisons on the basis of a specific study for each conveyor application.

As a general guide to conveyor selection, Table 21-1 indicates **conveyor choices** on the basis of some common functions. Table 21-2 is designed to aid in **feeder selection** on the basis of the physical characteristics of the material to be handled. Table 21-3 is a coded listing of **material characteristics** to be used with Table 21-4, which describes the conveying qualities of some common materials. While these tables may serve as valuable guides, conveyor selection must be based on the **as-conveyed characteristics** of a material. For instance, if packing or aerating can occur in the conveyor, the machine's performance will not meet expectations if calculations are based on an average weight per cubic meter. Storage conditions, variations in ambient temperature and humidity, and discharge methods may all affect conveying characteristics. Such factors should be carefully considered before making a final conveyor selection.

To obtain a reliable **measurement of bulk density,** any wide-mouthed vessel with a capacity of 1 ft^3 or more may be used. When such a determination must be made often, it is worthwhile to con-

TABLE 21-1 Conveyors for Bulk Materials*

Function	Conveyor type
Conveying materials horizontally	Apron, belt, continuous flow, drag flight, screw, vibrating, bucket, pivoted bucket, air
Conveying materials up or down an incline	Apron, belt, continuous flow, flight, screw, skip hoist, air
Elevating materials	Bucket elevator, continuous flow, skip hoist, air
Handling materials over a combination horizontal and vertical path	Continuous flow, gravity-discharge bucket, pivoted bucket, air
Distributing materials to or collecting materials from bins, bunkers, etc.	Belt, flight, screw, continuous flow, gravity-discharge bucket, pivoted bucket, air
Removing materials from rail cars, trucks, etc.	Car dumper, grain-car unloader, car shaker, power shovel, air

*From FMC Corporation, Material Handling Systems Division.

TABLE 21-2 Feeders for Bulk Materials*

Material characteristics	Feeder type
Fine, free-flowing materials	Bar flight, belt, oscillating or vibrating, rotary vane, screw
Nonabrasive and granular materials, materials with some lumps	Apron, bar flight, belt, oscillating or vibrating, reciprocating, rotary plate, screw
Materials difficult to handle because of being hot, abrasive, lumpy, or stringy	Apron, bar flight, belt, oscillating or vibrating, reciprocating
Heavy, lumpy, or abrasive materials similar to pit-run, stone, and ore	Apron, oscillating or vibrating, reciprocating

*From FMC Corporation, Material Handling Systems Division.

TABLE 21-3 Classification System for Bulk Solids*

	Material characteristics	Class
Size	Very fine—< 149 μm (100 mesh)	A
	Fine—149 μm to 3.18 mm (100 mesh to ⅛ in)	B
	Granular—3.18 to 12.7 mm (⅛ to ½ in)	C
	Lumpy—containing lumps > 12.7 mm (½ in)	D
	Irregular—being fibrous, stringy, or the like	H
Flowability	Very free-flowing—angle of repose up to 30°	1
	Free-flowing—angle of repose 30 to 45°	2
	Sluggish—angle of repose 45° and up	3
Abrasiveness	Nonabrasive	6
	Mildly abrasive	7
	Very abrasive	8
Special characteristics	Contaminable, affecting use or salability	K
	Hygroscopic	L
	Highly corrosive	N
	Mildly corrosive	P
	Gives off dust or fumes harmful to life	R
	Contains explosive dust	S
	Degradable, affecting use or salability	T
	Very light and fluffy	W
	Interlocks or mats to resist digging	X
	Aerates and becomes fluid	Y
	Packs under pressure	Z

*From FMC Corporation, Material Handling Systems Division.

Example: A material which is granular, very free-flowing, mildly abrasive, and mildly corrosive would fall in classes C, 1, 7, and P, making its classification C17P.

struct a test box from wood or light metal having a dimension of exactly 1 ft for length, width, and depth. The material to be weighed is poured into the test box to overfill it slightly. After the material has been leveled, the test box and its contents are weighed, and after adjustment has been made for the tare weight, the weight obtained is equivalent to the bulk density in the loose or flowing condition. If a loose density is to be determined, care should be exercised in filling the test box so as not to rap or vibrate the material. When a settled density is needed, the filling portion of the procedure is accompanied by rapping the walls of the box until no more material can be added. The density value obtained by this experiment (pounds per cubic foot) can be directly converted to SI units by multiplying by 16.02, giving density in kilograms per cubic meter.

Conveyor Drives Conveyor drives may account for from 10 to 30 percent of the total cost of the conveyor system, depending on specific job requirements. They may be of either fixed-speed or adjustable-speed type. **Fixed-speed drives** are used when the initially chosen conveyor speed does not require change during the course of normal operation. Simple sheave or sprocket changes suffice should minor speed alterations be needed. However, for major adjustments motor or speed-reducer changes are required. In any event, the conveyor must be shut down while the speed change is made. **Adjustable-speed drives** are designed for changing speed either manually or automatically while the conveyor is in operation, to meet variations in processing requirements.

The number of **speed reductions** is another way to classify conveyor drives. Most common of the speed-reduction methods is the two-step system, in which the motor is coupled to a speed reducer and the slow-speed shaft of the reducer is connected to the conveyor-drive shaft by a V belt or a roller chain. The second reduction not only permits the use of a simpler speed reducer but also allows a more flexible layout of the motor and reducer mounting plate. On many installations this eliminates the need for a specially designed drive mount.

Since it is good practice to maintain a selected inventory of spare parts for drives, economy can be achieved by **standardizing conveyor drives** throughout the plant. For example, intermediate speed reduction by means of V belts, sheaves or chains, and sprockets can frequently permit using the same speed-reducer size for several drives. Thus, it may be necessary to keep only one repair-stock speed reducer for a number of conveyors.

Conveyor Motors Motors for conveyor drives are generally three-phase, 60-Hz, 220-V units; 220/440-V; 550-V; four-wire, 208-V. Also common are 240- and 480-V ratings. Although many adjustable-speed drives use alternating-current induction motors, powered by ac alternators or ac-driven eddy-current clutches, there is a strong preference for direct-current motors when speed adjustments are required over a wide range at extremely accurate settings.

The **silicon-controlled rectifier** with a dc motor has become predominant in adjustable-speed drives for almost all commonly used conveyors when speed adjustment to process conditions is necessary. The low cost of this control device has influenced its use when speed synchronization among conveyors is required. This can also be done, of course, by changing sheave or sprocket ratios.

The **squirrel-cage motor** is most commonly used with belt conveyors and with drives up to 7.457 kW (10 hp); across-the-line starting is generally specified. Between 7.457 and 37.285 kW (10 and 50 hp), squirrel-cage motors are usually started by means of a manual reduced-voltage starter or a magnetic primary-resistance starter. Normal-torque motors are generally specified, with the assumption that if power is sufficient to drive the belt, sufficient starting torque can be developed. Motor selection for large conveyors should be based on a careful study, with particular emphasis on starting conditions.

Auxiliary Equipment Elevating conveyors must be equipped with some form of **holdback** or **brake** to prevent reversal of travel and subsequent jamming when power is unexpectedly cut off. Ratchet and wedge roller-type holdbacks are commonly used. Solenoid brakes and spring clutches may also be employed.

Another problem with most conveyors is to cut out the driving force when a conveyor jams. **Torque-limiting devices** are often used, as are electrical controls which cut power to the drive motor. However, because of the high inertia of the motor rotor, it is sometimes desirable to eliminate the torque surge which may occur when the conveyor jams. A shear-pin hub is generally used in these cases, power being transmitted through a set of pins which are designed to shear at a fixed maximum torque. While equipment remains down until the pins can be replaced, there is an immediate disconnect between motor and conveyor which may prevent serious equipment damage. Special clutches are also used.

Unless a material discharges freely, **cleaners** are required on belt conveyors and may be helpful on others. Common types use a rotating brush, powered from the conveyor head-pulley shaft or independently, or a spring-mounted blade. The latter is applicable only at some point where the belt conveyor lies reasonably flat. Whenever cleaners are used, provision should be made for catching and chuting the material back into the main discharge stream or to a collecting container which can be periodically emptied.

Control of Conveyors Control has been enhanced considerably with the introduction of process-control computers and programmable controllers, which can be used to maintain rated capacities to close tolerances. This ability is especially useful if feed to the conveyor tends to be erratic. Through variable-speed drives, outputs can be adjusted automatically for changes in processing conditions. When the control devices are used in conjunction with strain-gauge or load-cell weight-sensing devices, actual discharge rates can be measured and employed in process calculations made by these devices, and output adjustments can be made automatically and accurately.

SCREW CONVEYORS

The screw conveyor is one of the oldest and most versatile conveyor types. It consists of a helicoid flight (helix rolled from flat steel bar) or a sectional flight (individual sections blanked and formed into a helix from flat plate), mounted on a pipe or shaft and turning in a trough. Power to convey must be transmitted through the pipe or shaft and is limited by the allowable size of this member. Screw-conveyor capacities are generally limited to around 4.72 m^3/min (10,000 ft^3/h).

In addition to their conveying ability, screw conveyors can be adapted to a wide variety of **processing operations.** Almost any degree of mixing can be achieved with screw-conveyor flights cut, cut and folded, or replaced by a series of paddles. Use of ribbon flights allows sticky materials to be handled. Variable-pitch, tapered-flight, or stepped-flight units can give excellent control for feeder applications

TABLE 21-4 Material Classes and Bulk Densities*

Material	Average bulk density, lb/ft³†	Class‡	Material	Average bulk density, lb/ft³†	Class‡
Alum, lumpy	50–60	D26§	Lime, ground, ⅛ in and under	60	B36Z
Alum, fine	45–50	B26§	Lime, hydrated, ⅛ in and under	40	B26YZ
Alumina	60	B28	Lime, hydrated, pulverized	32–40	A26YZ
Alumina gel	45	B27	Lime, pebble	53–56	D36
Aluminum hydrate	18	C26	Limestone, agricultural, ⅛ in and under	68	B27§
Ammonium chloride, crystalline	52	B26	Limestone, crushed	85–90	D27§
Ammonium sulfate	45–58	§	Limestone dust	75	A37Y§
Antimony powder		B27	Magnesium chloride	33	C36
Asbestos shred	20–25	H37WZ	Manganese sulfate	70	C28
Ashes, coal, dry, 3 in. and under	35–40	D37	Marl	80	D27§
Asphalt, crushed, ½ in and under	45	C26	Mica, flakes	17–22	B17WY
Bagasse	7–10	H36WXZ	Mica, ground	13–15	B27
Baking powder	41	A26	Mica, pulverized	13–15	A27Y
Bark, wood, refuse	10–20	H37X§	Muriate of potash	77	B28
Bauxite, crushed, 3 in and under	75–85	D28§	Naphthalene flakes	45	§
Bentonite, 100 mesh and under	50–60	A27Y§	Oxalic acid crystals	60	B36L
Bicarbonate of soda	41	A26	Oyster shells, ground, ½ in and under	53	C27
Boneblack, 100 mesh and under	20–25	A27§	Oyster shells, whole		D27X
Bonechar, ⅛ in and under	27–40	B27	Phenol-formaldehyde molding powder	30–40	A36
Bonemeal	55–60	B27	Phosphate rock	75–85	D27§
Borate of lime		A26§	Phosphate sand	90–100	B28
Borax, fine	53	B26	Phthalic anhydride flakes	30–35	C36XZ
Boric acid, fine	55	B26	Polyethylene pellets, high-density	35–45	C16K
Calcium carbide	70–80	D27	Polyethylene pellets, low-density	28–40	C16K
Carbon black, pelletized	20–25	B16TZ§	Polypropylene pellets	35–50	C16K
Carbon black, powder	4–6	§	Polystyrene cubes	35–40	C16K
Casein	36	B27§	Polyvinyl chloride pellets, compounds	35–55	C16K
Cast-iron chips	130–200	C37	Polyvinyl chloride resin, dispersion-type	12–18	A36KPY
Cement, Portland	65–85	A27Y	Polyvinyl chloride resin, solvent, non-solvent, suspension types	20–35	A26KY
Cement clinker	75–80	D28§	Potassium nitrate	76	C17P
Chalk, lumpy	85–90	D37Z	Pumice, ⅛ in and under	42–45	B38§
Chalk, 100 mesh and under	70–75	A37YZ	Salt, common dry, coarse	45–50	C37PL§
Charcoal	18–25	D37T	Salt, common dry, fine	70–80	B27PL§
Cinders, coal	40	D28§	Salt cake, dry, coarse	85	D27
Clay (see bentonite, fuller's earth, kaolin, and marl)			Salt cake, dry, pulverized	65–85	B27
Coal, anthracite	60	C27P	Saltpeter	80	B26S
Coal, bituminous, mined, 50 mesh and under	50	B36P	Sand, bank, dry	90–110	B28
Coal, bituminous, mined, sized	50	D26PT	Sand, silica, dry	90–100	B18
Coal, bituminous, mined, slack, ½ in and under	50	C36P	Sawdust	10–13	§
Coke, loose	23–32	D38TX§	Shale, crushed	85–90	C27
Coke, petroleum, calcined	35–45	D28X	Shellac, powdered or granulated	31	B26K§
Coke breeze, ¼ in and under	25–35	C38	Silica gel	45	B28
Copper sulfate		D26	Slag, furnace, granulated	60–65	C28
Cork, fine ground	12–15	B36WY	Slate, crushed, ½ in and under	80–90	C27
Cork, granulated	12–15	C36	Slate, ground, ⅛ in and under	82	B27
Cryolite	110	D27	Soap beads or granules		B26T
Cullet	80–120	D28§	Soap chips	15–25	C26T§
Dicalcium phosphate	43	A36	Soap flakes	5–15	B26T§
Dolomite, lumpy	90–100	D27§	Soap powder	20–25	B26§
Ebonite, crushed, ½ in and under	63–70	C26	Soapstone talc, fine	40–50	A37Z
Epsom salts	40–50	B26	Soda ash, heavy	55–65	B27
Feldspar, ground, ⅛ in and under	65–70	B27	Soda ash, light	20–35	A27W
Ferrous sulfate	50–75	C27	Sodium nitrate	70–80	§
Flour, wheat	35–40	A36K§	Sodium sulfate (see salt cake)		
Fluorspar	82	C37	Starch	25–50	§
Fly ash, dry	35–45	A18Y§	Steel chips, crushed	100–150	D38
Fuller's earth, oil filter, burned	40	B28	Sugar, granulated	50–55	B26KT
Fuller's earth, oil filter, raw	35–40	B27	Sugar, raw, cane, or beet	55–65	B36Z§
Fuller's earth, oil filter, spent	60–65	§	Sugar-beet pulp, dry	12–15	§
Glass batch	90–100	D28§	Sugar-beet pulp, wet	25–45	§
Glue, ground, ⅛ in and under	40	B27	Sulfur, crushed, ½ in and under	50–60	C26S§
Graphite, flake	40	C26	Sulfur, lumpy, 3 in and under	80–85	D26S§
Graphite, flour	28	A16Y	Sulfur, powdered	50–60	B26SY§
Gypsum, calcined, ½ in and under	55–60	C27	Talcum powder	40–60	A27Y
Gypsum, calcined, powdered	60–80	A37	Trisodium phosphate	60	B27
Gypsum, raw, 1 in and under	90–100	D27	Vermiculite, expanded	16	C37W
Ice, crushed	35–45	D16	Vermiculite ore	80	D27
Ilmenite	140	B28	Wood chips	10–30	H36WX§
Kaolin clay, 3 in and under	163	D27	Wood flour	16–36	§
Lead arsenate	72	B36R	Zinc oxide, heavy	30–35	A36Z§
Lignite, air dried	45–55	D26	Zinc oxide, light	10–15	A36WZ§

*Data supplied mostly by FMC Corporation, Material Handling Systems Division. To convert pounds per cubic foot to kilograms per cubic meter, multiply by 16.02.
†Weights of material, loose or slightly agitated. Weights are usually different when materials are settled or packed as in bins or containers.
‡These classes represent observations under general conditions. Specific conditions may vary because of manufacturing processes and handling.
§Class may vary considerably because of conditions.

or on conveyors when precise control of the transport rate is required. Short-pitch screws are used for inclined and vertical conveying applications, and double-flight short-pitch units effectively deter flushing action. In addition to a wide variety of designs for components, screw conveyors may be fabricated in materials ranging from cast iron to stainless steel.

Use of hollow screws and pipes for circulating hot or cold fluids allows the screw conveyor to be used for heating, cooling, and drying operations. Jacketed casings may be used for the same purpose. It is relatively easy to seal a screw conveyor from the outside atmosphere so that it can operate outdoors without special protection. In fact, the conveyor can be completely sealed to operate in its own atmosphere at positive or negative pressure, and the casing can be insulated to maintain internal temperatures in areas of high or low ambient temperature. A further advantage is the fact that the casing can be designed with a drop bottom for easy cleaning to avoid contamination when different materials are to be run through the same system.

Since screw conveyors are usually made up of standard sections coupled together, special attention should be given to bending stresses in the couplings. Hanger bearings supporting the flights obstruct the flow of material when the trough is loaded above their level. Thus, with difficult materials, the load in the trough must be kept below this level, or special hanger bearings which minimize obstruction should be selected. Since screw conveyors operate at relatively low rotational speeds, the fact that the outer edge of the flight may be moving at a relatively high linear speed is often neglected. This may create a wear problem; if wear is too severe, it can be reduced by the use of hard-surfaced edges, detachable hardened flight segments, rubber covering, or high-carbon steels.

Power calculations for screw conveyors are well standardized. However, each manufacturer has grouped numerical constants in a different fashion and assigned slightly different values on the basis of individual design variations. Thus, in comparing screw-conveyor power requirements it is advisable to use a specific formula for specific equipment.

Required power is made up of two components, that necessary to drive the screw empty and that necessary to move the material. The first component is a function of conveyor length, speed of rotation, and friction in the conveyor bearings. The second is a function of the total weight of material conveyed per unit of time, conveyed length, and depth to which the trough is loaded. The latter power item is in turn a function of the internal friction and friction on metal of the conveyed material.

Table 21-5 indicates **screw-conveyor performance** on the basis of material classifications as listed in Table 21-4 and defined in Table 21-3. Table 21-6 gives a wide range of **capacities** and **power requirements** for various sizes of screws handling 801 kg/m^3 (50 lb/ft^3) of material of average conveyability. Within reasonable limits, values from Tables 21-5 and 21-6 can be interpolated for preliminary estimates and designs.

Typical **feed arrangements** are shown in Fig. 21-1. Plain spouts (Fig. 21-1*a*) may be used when the feed rate is fairly uniform and controlled by preceding equipment. The capacity of the conveyor should be well above the maximum rate of feed from either single or multiple feed points. The rotary cutoff valve (Fig. 21-1*b*) is an enclosed dust-tight quick-acting valve for free-flowing materials. The rotary-vane feeder (Fig. 21-1*c*) delivers a uniform predetermined volume of material and may be driven from the screw or independently by constant- or variable-speed drive. Rack-and-pinion gates (Fig. 21-1*d*) are well suited to free-flowing materials in bins, hoppers, tanks, or silos and are also used as side inlet gates (Fig. 21-1*e*) for heavy or lumpy materials.

Typical **discharge arrangements** are shown in Fig. 21-2. Plain discharge openings (Fig. 21-2*a*) equipped with a discharge spout (Fig. 21-2*b*) are most common, although the open-end trough (Fig. 21-2*c*) is frequently used, as is the discharge-trough end (Fig. 21-2*e*). Open-bottom troughs (Fig. 21-2*g*) are often used for spreading material uni-

TABLE 21-5 Screw-Conveyor Capacities and Loading Conditions*

Material class†	Screw diam., in	Max. lump size, in		Capacity, cu ft/hr‡		Approx. area occupied by material¶
		25% lumps	100% lumps	At 1 rpm.	At max. rpm.§	
A, B, C, D, and H 16, 26, 36	6	¾	½	2.27	375	 45%
	9	1½	¾	8.0	1,200	
	12	2	1	19.3	2,700	
	14	2½	1¼	30.8	4,000	
	16	3	1½	46.6	5,600	
	18	3	2	66.1	7,600	
	20	3½	2	95.0	10,000	
A, B, C, D, and H 17, 27, 37	6	¾	½	1.5	75	 30%
	9	1½	¾	5.6	280	
	12	2	1	13.3	665	
	14	2½	1¼	21.1	1,055	
	16	3	1½	31.4	1,570	
	18	3	2	45.4	2,270	
	20	3½	2	62.1	3,105	
A, B, C, D, and H 18, 28, 38	6	¾	½	0.75	25	 15%
	9	1½	¾	2.8	90	
	12	2	1	6.7	200	
	14	2½	1¼	10.5	300	
	16	3	1½	15.7	425	
	18	3	2	22.7	590	
	20	3½	2	31.1	780	

*FMC Corporation, Material Handling Systems Division. To convert cubic feet per hour to cubic meters per hour, multiply by 0.02832; to convert screw diameter in inches to the nearest screw size in centimeters, multiply by 2.5. See elsewhere for conversion of particle sizes from one measurement system to another.

†These classifications cover a broad list of materials that generally can be handled in a screw conveyor. Special consideration must be given to applications handling materials with the following characteristics:
Highly corrosive, Class N
Degradable, affecting use or salability, Class T
Interlocks or mats, Class X
Highly aerated or of fluid nature, Class Y

‡Capacity for horizontal conveyor uniformly fed. Volumetric capacity is based on material slightly agitated or fluffed. Material highly fluffed or aerated will decrease in weight and increase in volume.

§Maximum capacity for economical service.

¶Percentages higher than those indicated will result in excessive wear on hanger bearings and couplings.

TABLE 21-6 Screw-Conveyor Data for 50-lb/ft³ Material and Pipe-Mounted Sectional Spiral Flights*

Capacity†		Diam. of flights, in	Diam. of pipe, in‡	Diam. of shafts, in	Hanger centers, ft	Max. size of lumps			Speed, r/min	Max. torque capacity, in·lb	Feed section diam., in	hp at motor§					Max. hp capacity at speed listed
Tons/h	ft³/h					All lumps	Lumps 20 to 25%	Lumps 10% or less				15-ft. max. length	30-ft max. length	45-ft max. length	60-ft max. length	75-ft max. length	
5	200	9	2½	2	10	¾	1½	2¼	40	7,600	6	0.43	0.85	1.27	1.69	2.11	4.8
10	400	10	2½	2	10	¾	1½	2½	55	7,600	9	0.85	1.69	2.25	3.00	3.75	6.6
15	600	10	2½	2	10	¾	1½	2½	80	7,600	9	1.27	2.25	3.38	3.94	4.93	9.6
		12	2½	2	12	1	2	3	45	7,600	10	1.27	2.25	3.38	3.94	4.93	5.4
		12	3½	3						16,400		1.27	2.25	3.38	3.94	4.93	11.7
20	800	12	2½	2	12	1	2	3	60	7,600	10	1.69	3.00	3.94	4.87	5.63	7.2
			3½	3						16,400		1.69	3.00	3.94	4.87	5.63	15.6
25	1000	12	2½	2	12	1	2	3	75	7,600	10	2.12	3.75	4.93	5.63	6.55	9.0
			3½	3						16,400		2.12	3.75	4.93	5.63	6.55	9.0
		14	3½	3		1¼	2½	3½	45	16,400	12	2.12	3.75	4.93	5.63	6.55	11.7
30	1200	14	3½	3	12	1¼	2½	3½	55	16,400	12	2.25	3.94	5.05	6.75	7.50	14.3
35	1400	14	3½	3	12	1¼	2½	3½	65	16,400	12	2.62	4.58	5.90	7.00	8.75	16.9
40	1600	16	3½	3	12	1½	3	4	50	16,400	14	3.00	4.50	6.75	8.00	10.00	13.0

*Fairfield Engineering Co. data in U.S. customary system. To convert cubic feet per hour to cubic meters per hour, multiply by 0.02832; to convert tons per hour to metric tons per hour, multiply by 0.9078; and to convert screw size in inches to the nearest screw size in centimeters, multiply by 2.5.

†Capacities are based on screws carrying 31 percent of their cross section and, in the case of feed sections with half-pitch flights, based on 100 percent of their cross section.

‡Pipe sizes given are for ¼-in (6.35-mm) flights.

§Horsepowers listed are calculated for average conditions and are of the proper motor size with factors for length of conveyor, momentary overloads, etc., taken into consideration.

formly over a storage area. Flat-bottomed rack-and-pinion gates (Fig. 21-2*f*) allow selective discharge, as do hand slide gates (Fig. 21-2*d*). However, for perishable materials, the curved slide gate (Fig. 21-2*h*) eliminates the dead-storage pocket. Enclosed rack-and-pinion gates (Fig. 21-2*j*) give dust-tight operation, and rotary cutoff valves (Fig. 21-2*i*) allow quick shutoff and are readily adaptable to remote control. Air-cylinder-actuated gates have become more and more prominent because of the low investment required and the ease of connecting to automatic process-control centers.

BELT CONVEYORS

The belt conveyor is almost universal in application. It can travel for miles at speeds up to 5.08 m/s (1000 ft/min) and handle up to 4539 metric tons/h (5000 tons/h). It can also operate over short distances at speeds slow enough for manual picking, with a capacity of only a few kilograms per hour. However, it is not normally applicable to processing operations, except under unusual conditions.

Belt-conveyor slopes are limited to a maximum of about 30°, with those in the 18 to 20° range more common. Direction changes can occur only in the vertical plane of the belt path and must be carefully designed as vertical curves or relatively flat bends. Belt conveyors inside the plant may have higher initial cost than some other types of conveyors and, depending on idler design, may or may not require more maintenance. However, a belt conveyor given good routine maintenance can be expected to outlast almost any other type of conveyor. Thus, in terms of cost per ton handled, outstanding economy records have been established by belt conveyors.

Belt-conveyor design begins with a study of the material to be handled. Since weight per cubic meter or foot is an important factor, it should be accurately determined with the material in an as-handled condition. It is not wise to rely solely on published tables of weight per cubic meter or foot for various materials, since many processing operations will affect this by fluffing or compacting the material. Lump size is important, too. For a 600-mm (24-in) belt, uniform lump size can range up to about 102 mm (4 in). For each 152-mm (6-in) increase in belt width, lump size can increase by about 51 mm (2 in). If material contains around 90 percent fines, lump size can be increased by around 50 percent. However, care should be taken to maintain uniform flow of material, with fine material reaching the belt first to protect it from impact damage. The larger the lump, the more danger of its falling off the belt or rolling back on inclines. With the belt running horizontally or sloping only slightly at the feed point, the problem of lumps falling off is minimized, especially if particular care is taken with feed-chute design.

Temperature and chemical activity of the conveyed material play important roles in **belt selection.** For example, natural rubber should be avoided with oily materials even when the material does not present an obviously oily surface. Special rubber, cotton, and asbestos-fiber belts are available to meet varying degrees of material temperature, and they should be used whenever high temperatures exist. Belts can be seriously and quickly damaged by high temperature, and the investment in what at first glance seems to be an extremely high-priced belt may prove most economical in the long run. There are many superperformance elastomers available for belt construction. These include neoprene, Teflon, Buna N rubber, and vinyls. Manufacturers are able to test products to be handled and often recommend several elastomer grades that will perform satisfactorily, each grade having a different first-cost–operating-life relation.

Moisture may create poor discharge conditions because of material sticking to the belt and to chutes, or it may even reduce capacity if it is present in enough quantity to give the material fluid properties. Even though abrasion may create problems with belt conveyors, these are easier to solve with properly designed belt systems than with most other conveyors.

In establishing belt-conveyor **tonnage requirements** it is important to work with peak rather than average loads. Only occasionally, because of intentional or accidental variations in production rates, are these two figures identical. The belt that runs empty half the time must carry twice the average load when it is working.

When a belt conveyor must **change direction,** it is often easier to use more than one conveyor. However, vertical curves can be designed and upward changes of direction accomplished with a pair of snub pulleys. If the belt pull is downward on the idlers, a simple flat pulley can be used for minor directional changes. In any case, using a single continuous belt eliminates the need for more than one drive. With a pair of snub pulleys, the carrying face of the belt is brought in contact with the pulley; hence special care must be taken to get a good discharge. When bending the belt over a flat pulley, belt speed must be slow enough to keep material from flying off the belt. In many situations the smooth curve, either concave or convex, is preferable. For a 61-cm (24-in) belt the minimum curve radius is about 61 m (200 ft),

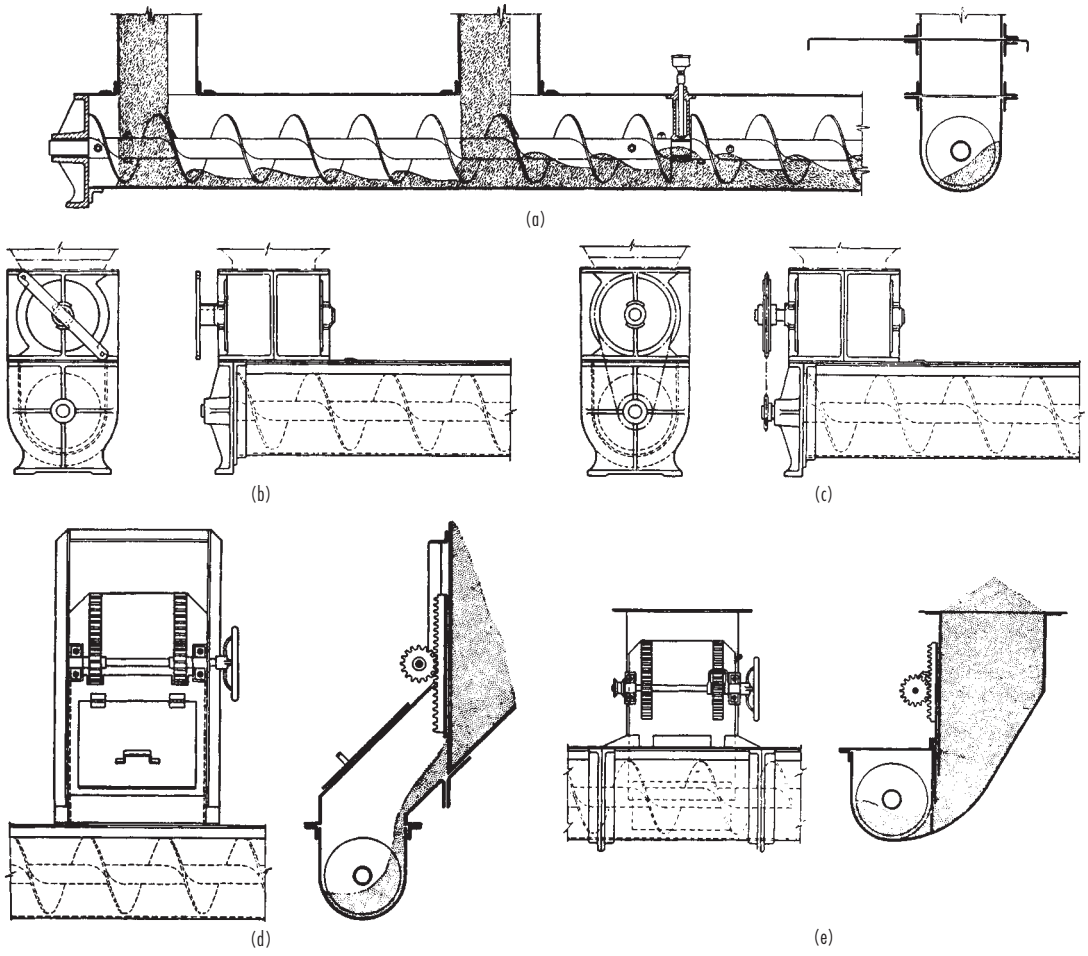


FIG. 21-1 Typical feed arrangements for screw conveyors. (*a*) Plain spouts of chutes. (*b*) Rotary cutoff valve. (*c*) Rotary-vane feeder. (*d*) Bin gate. (*e*) Side inlet gate. (*FMC Corporation, Material Handling Systems Division.*)

but for best operating conditions the curve should be carefully designed.

Operating conditions which affect belt-conveyor design include climate, surroundings, and hours of continuous service. Temperature and humidity extremes may dictate total enclosure of the belt; surroundings which involve such conditions as high temperature or corrosive atmosphere can affect belt, machinery, and structure; and continuous service may require extremely high-quality components and even specially designed equipment for servicing while the belt is in operation. For example, idlers may be obtained with tilting stands which allow them to be tipped out of the way for service while the belt is running.

Belt width and **speed** are functions of bulk density of the material and lump size. Lowest first cost can often be obtained by using the narrowest possible belt for a given lump size and operating it at maximum speed. However, speed often may be limited by dusting, and sometimes it may be better economy to use a wider belt with fewer plies to combine the necessary tensile strength with good belt-troughing characteristics. Abrasiveness of the material can strongly affect speed and also lump size, for at higher speeds abrasive wear is increased and there is greater danger of lumps rolling off the belt. Ideally a belt should run with lump size, slope, and load of less than recommended maximums and with uniform feed introduced to the belt centrally as nearly as possible in the direction and speed of belt travel.

Power to drive a belt conveyor is made up of five components: power to drive the empty belt, to move the load against friction of the rotating parts, to raise or lower the load, to overcome inertia in putting material into motion, and to operate a belt-driven tripper if required. As with most other conveyor problems, it is advisable to work with formulas and constants from a specific manufacturer in making these calculations. For estimating purposes, typical data are given in Table 21-7.

Belt selection depends on power and development of the required tensile strength. Knowing drive-shaft power, belt tension can be calculated and a belt selected. However, since various combinations of width and ply thickness will develop the required strength, final selection is influenced by lump size, troughability of the belt, and ability of the belt to support the load between idlers. Thus it is necessary to use an empirical approach to arrive at a belt selection which meets all requirements.

Once final belt selection has been made, **idlers** and **return rolls** can also be selected. Figure 21-3 indicates the wide variety of belt supports for bulk-handling applications. Figure 21-3*a* and *b* consists of flat-belt arrangements of rollers or plate which allow material to be discharged by simple V-shaped plows. The flat plate-supported belt allows sidewalls to be erected to prevent dribble or to build up larger loads on the flat belt. As in Fig. 21-3*f*, larger capacity can also be achieved by troughing the plate. The 20° troughing idler with equal-length rolls (Fig. 21-3*c*) is the most common, with lighter materials adaptable to 45° idlers with short or long side rolls (Fig. 21-3*d* and *e*).

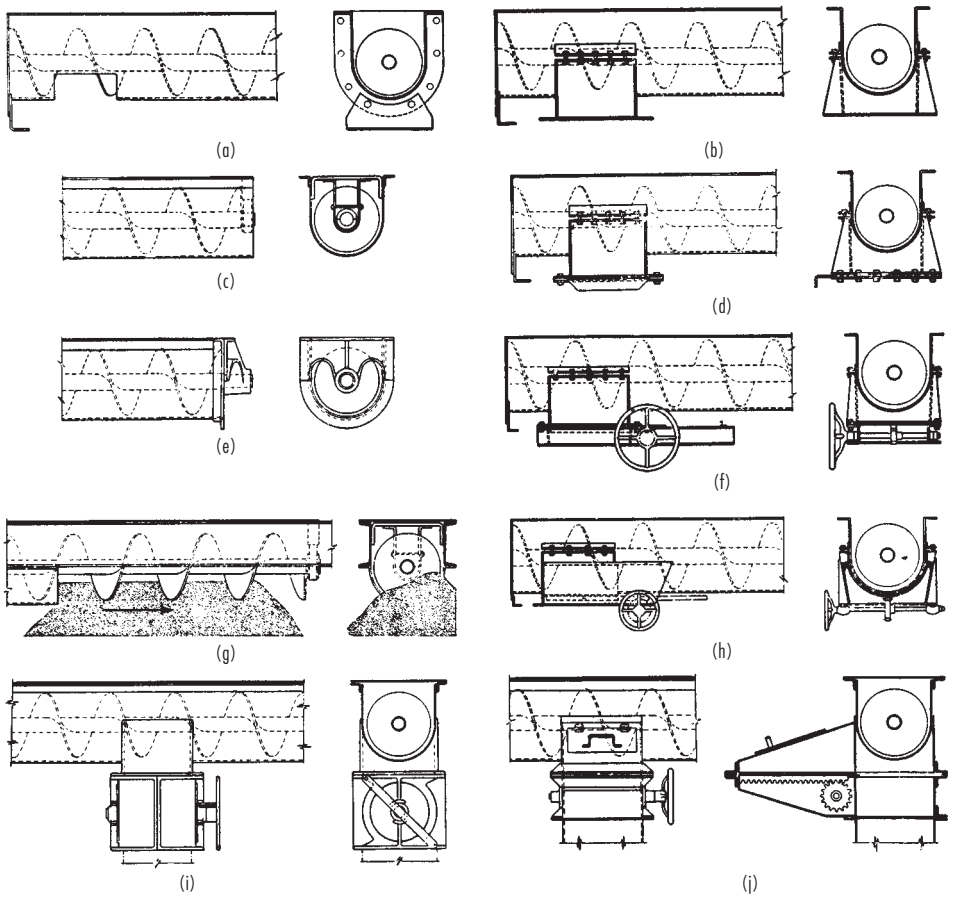


FIG. 21-2 Typical discharge arrangements for screw conveyors. (*a*) Plain discharge opening. (*b*) Discharge spout. (*c*) Open-end trough. (*d*) Hand slide gate. (*e*) Discharge trough end. (*f*) Rack-and-pinion flat side gate. (*g*) Open-bottom trough. (*h*) Rack-and-pinion curved slide gate. (*i*) Rotary cutoff valve. (*j*) Enclosed rack-and-pinion gate. (*FMC Corporation, Material Handling Systems Division.*)

Since the lighter materials do not require stiff belts for tensile strength, there is usually no problem with troughing.

With the proper idlers selected for size and service conditions, the most important step is to locate them properly. For long belts the tension varies considerably, and idlers should be spaced to hold belt sag to reasonable limits along the full length of travel. Too much belt sag can cause a significant power loss, but for most belts of ordinary length it is usually satisfactory to space idlers fairly closely at the feed point and then farther apart and uniformly for the rest of the conveyor length.

Loading and discharge points on belt conveyors need to accommodate several factors. Figure 21-4*a* shows details for one type of rubber seal on a metal skirt plate. It is particularly important that material be loaded onto the belt in its center and in the direction of its travel, preferably with lumps falling on a layer of fine material. Fines can be delivered to the belt first by notching the feed chute or installing a screen section or grizzly bars. Figure 21-4*b* shows a heavy-duty loading-section design using not only rubber idler rolls but an additional short pad belt. Mass-flow bins and/or bin-flow-assisting devices are often used to minimize segregation of fines and to assure a uniform feed from a hopper onto a conveyor belt.

A clean discharge is vital to good belt life. On the return run the carrying side of the belt is in contact with the return rollers, and any material adhering to it is ground in or deposited on the roller. Extremely sticky material may require a belt-cleaning device in the form of a revolving brush, spring-mounted steel scrapers, rubber scraper blades, or sometimes a taut wire. When these devices are used, care should be taken that the dribble does not fall on the belt. Refer to the subsection "Storage and Weighing of Solids in Bulk," which deals with the criteria for bin design. For non-free-flowing materials, the combination of correct bin-discharge design and feeder-loading design is often a critical relation in which a slight error in either may produce a system in which the material will not flow at all.

BUCKET ELEVATORS

Bucket elevators are the simplest and most dependable units for making vertical lifts. They are available in a wide range of capacities and may operate entirely in the open or be totally enclosed. The trend is toward highly standardized units, but for special materials and high capacities it is wise to use specially engineered equipment. Main variations in quality are in casing thickness, bucket thickness, belt or chain quality, and drive equipment.

Spaced-Bucket Centrifugal-Discharge Elevators These elevators (Fig. 21-5*a*) are the most common. They are usually equipped with the style 1 or 2 buckets shown in Fig. 21-5*h*. Mounted on a belt or a chain, the buckets are spaced to prevent interference in loading or discharging. This type of elevator will handle almost any free-flowing fine or small-lump material such as grain, coal, or dry chemicals. Buckets are loaded partly by material flowing directly into them

TABLE 21-7 Belt-Conveyor Data for Troughed Antifriction Idlers*

Belt width	Cross-sectional area of load	Belt speed, ft/min (m/min)		Belt plies		Maximum lump size, in (mm)		Capacity and hp for 100-lb/ft³ material				
						Sized material, 80% under	Unsized material, not over 20%	Belt speed, ft/min (m/min)	Capacity tons/h (metric tons/h)	hp/10-ft (3.05-m) lift	hp/100-ft (30.48-m) centers	Add for tripper hp†
14 (35)	0.11 (.010)	200 (61)	300 (91)	3	5	2.0 (51)	3.0 (76)	100 (30.5)	32 (29)	0.34	0.44	
								200 (61.0)	64 (58)	0.68	0.68	2.0
								300 (91.5)	96 (87)	1.04	1.32	
16 (40)	0.14 (.013)	200 (61)	300 (91)	3	5	2.5 (64)	4.0 (102)	100 (30.5)	44 (40)	0.46	0.56	
								200 (61.0)	88 (80)	0.90	1.12	2.5
								300 (91.5)	132 (120)	1.36	1.68	
18 (45)	0.18 (.017)	250 (76)	350 (107)	4	6	3.0 (76)	5.0 (127)	100 (30.5)	54 (49)	0.58	0.70	
								250 (76.2)	134 (122)	1.42	1.76	3.0
								350 (106.7)	190 (172)	2.00	2.42	
20 (50)	0.22 (.020)	250 (76)	350 (107)	4	6	3.5 (89)	6.0 (152)	100 (30.5)	66 (60)	0.70	0.84	
												3.20
								250 (76.2)	164 (148)	1.72	2.06	
								350 (106.7)	230 (209)	2.44	2.90	
24 (60)	0.33 (.030)	300 (91)	400 (122)	4	7	4.5 (114)	8.0 (203)	100 (30.5)	98 (89)	1.02	1.02	
								300 (91.5)	294 (267)	3.06	3.04	3.5
								400 (121.9)	392 (356)	4.08	4.04	
30 (75)	0.53 (.049)	300 (91)	450 (137)	4	8	7.0 (178)	12.0 (305)	100 (30.5)	158 (143)	1.60	1.50	
								300 (91.5)	474 (430)	4.80	4.50	5.0
								450 (137.2)	710 (645)	7.20	6.74	
36 (90)	0.78 (.072)	400 (122)	600 (183)	4	9	8.0 (203)	15.0 (381)	100 (30.5)	230 (209)	2.44	1.59	
								400 (121.9)	920 (835)	9.74	6.36	7.0
								600 (182.9)	1380 (1253)	14.60	9.52	
42 (105)	1.09 (.101)	400 (122)	600 (183)	4	10	10.0 (254)	18.0 (457)	100 (30.5)	330 (300)	3.50	2.28	
								400 (121.9)	1320 (1198)	14.00	9.12	9.5
								600 (182.9)	1980 (1797)	23.20	13.68	
48 (120)	1.46 (.136)	400 (122)	600 (183)	4	12	12.0 (305)	21.0 (533)	100 (30.5)	440 (399)	4.66	3.04	
								400 (121.9)	1760 (1598)	18.70	12.14	12.8
								600 (182.9)	2640 (2397)	28.00	18.20	
54 (135)	1.90 (.177)	450 (137)	600 (183)	6	14	14.0 (356)	24.0 (610)	100 (30.5)	570 (517)	6.04	3.94	
								450 (137.2)	2564 (2328)	27.20	17.70	20.0
								600 (182.9)	3420 (3105)	36.20	23.60	
60 (150)	2.40 (.223)	450 (137)	600 (183)	6	16	16.0 (406)	28.0 (711)	100 (30.5)	720 (654)	7.64	4.98	
								450 (137.2)	3240 (2941)	34.40	22.40	23
								600 (182.9)	4320 (3921)	45.80	29.90	

*Fairfield Engineering Co. data in U.S. customary system. Metric conversion is rounded off. For inclined conveyors, add lift horsepower to center horsepower for total horsepower. For terminals multiply horsepower by the following factors: 0–50 ft (15.2 m), 1.20; 51–100 ft (30.5 m), 1.10; 101–150 ft (45.7 m), 1.05. For countershaft drives, multiply horsepower by 1.05 for each reduction (cut gears).

†Tripper horsepower is based on material bulk density of 100 lb/ft³ (1602 kg/m³) and a belt speed of 300 ft/min (91.4 m/min).

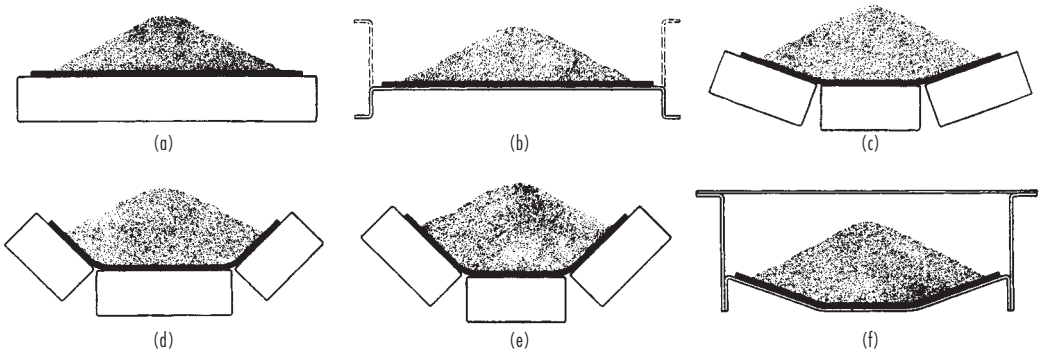
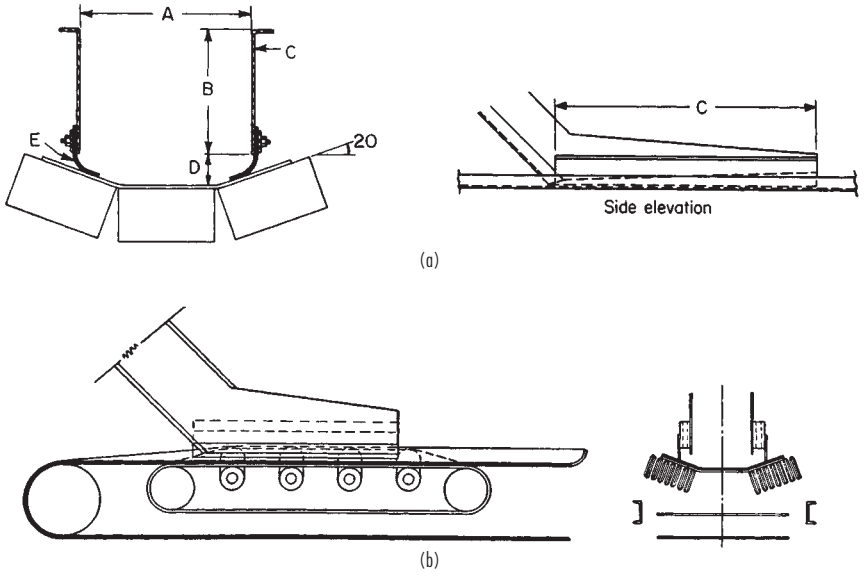


FIG. 21-3 Typical belt-conveyor idler and plate-support arrangements. (*a*) Flat belt on flat-belt idlers. (*b*) Flat belt on continuous plate. (*c*) Troughed belt on 20° idlers. (*d*) Troughed belt on 45° idlers with rolls of unequal length. (*e*) Troughed belt on 45° idlers with rolls of equal length. (*f*) Troughed belt on continuous plate. (*FMC Corporation, Material Handling Systems Division.*)



Skirt Plate and Seal Dimensions

Symbol	Name	Dimensions
A	Trough width	See table for (*a*).
B	Skirt depth	Minimum: 6 in (150 mm); maximum: 12 in (300 mm)
C	Skirt length	Minimum: 6 ft (1.8 m); maximum: 8 ft (2.4 m)
D	Skirt-to-belt clearance	See table for (*a*).
E	Seal specification	0.25-in- (6-mm-) thick live rubber, 6 in (150 mm) × *C*

Belt width, in (cm)	14 (35)	16 (40)	18 (45)	20 (50)	24 (60)	30 (75)	36 (90)	42 (110)	48 (125)	54 (140)	60 (155)
Trough width *A*, in (cm)	9 (23)	11 (28)	12 (30)	13 (33)	16 (41)	20 (51)	24 (61)	28 (71)	32 (81)	36 (91)	40 (102)
Skirt seal *D*, in (cm)	2.0 (5.1)	2.25 (5.7)	2.25 (5.7)	2.88 (7.3)	2.88 (7.3)	3.13 (8.0)	3.63 (9.2)	4.0 (10.1)	4.38 (11.1)	4.75 (12.1)	5.25(13.3)

FIG. 21-4 Belt-conveyor loading details. (*a*) Typical skirt-plate design and dimensions. (*b*) Pad belt and special roller-bearing idlers for heavy-duty loading. (*Stephens-Adamson Division, Allis-Chalmers Corporation.*)

and partly by scooping material from the boot as shown in Fig. 21-5*e*. Speeds can be relatively high for fairly dense materials but must be lowered considerably for aerated or low-bulk-density materials [under 641 kg/m^3 (40 lb/ft^3)] to prevent fanning action.

Spaced-Bucket Positive-Discharge Elevators Elevators of this type (Fig. 21-5*b*) are essentially the same as centrifugal-discharge units except that the buckets are mounted on two strands of chain and are snubbed back under the head sprocket to invert them for positive discharge. These units are designed especially for materials which are sticky or tend to pack, and the slight impact of the chain seating on the snub sprocket combined with complete bucket inversion is generally sufficient to empty the buckets completely. In extreme cases, knockers may be used to hit the buckets at the discharge point to help free material. The speed of these units is relatively slow, and buckets must be larger or more closely spaced to reach capacity levels of the centrifugal style.

Continuous-Bucket Elevators These elevators (Fig. 21-5*c*) are generally used for larger-lump materials or for materials too difficult

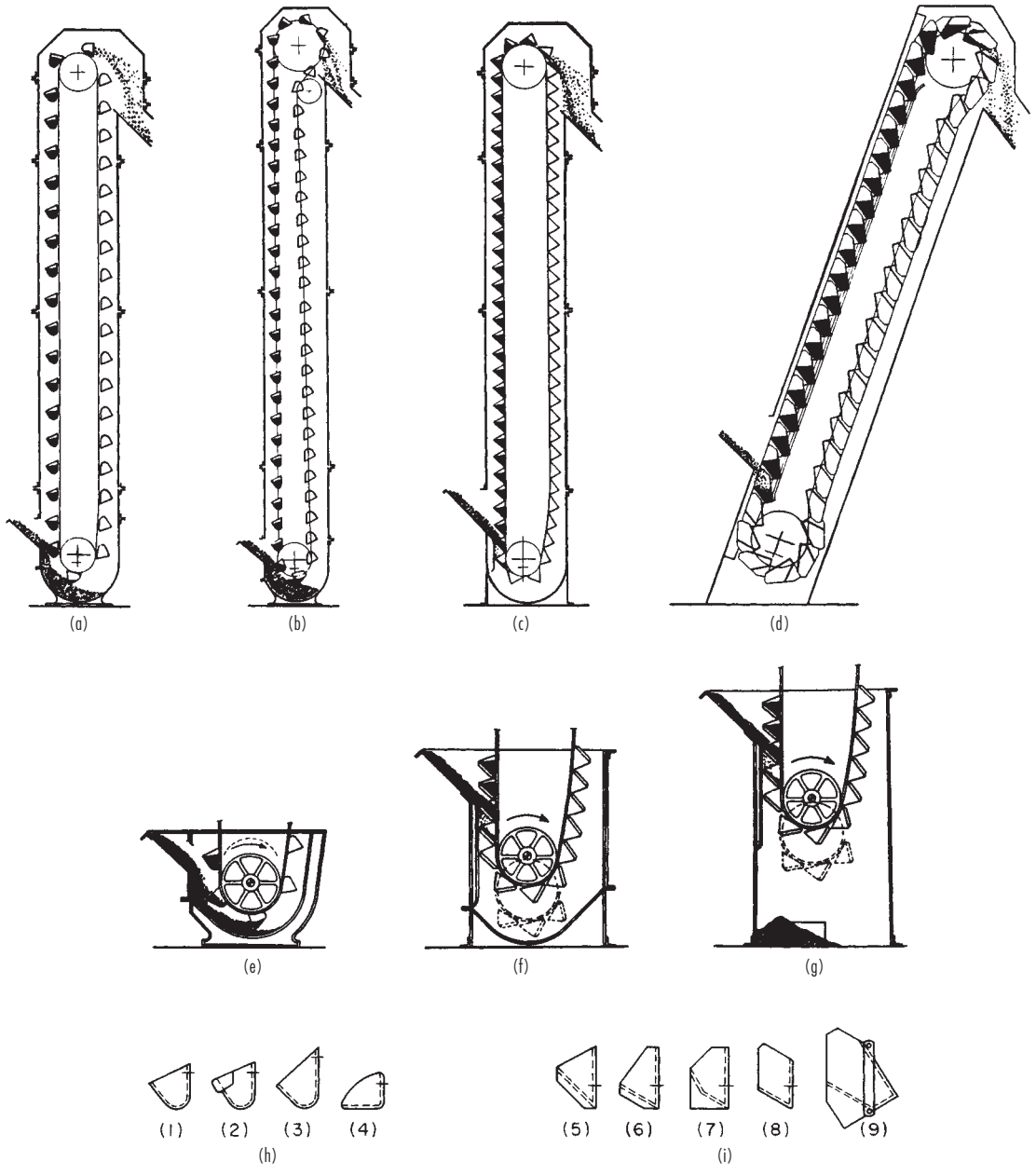


FIG. 21-5 Bucket-elevator types and bucket details. (*a*) Centrifugal-discharge spaced buckets. (*b*) Positive-discharge spaced buckets. (*c*) Continuous bucket. (*d*) Supercapacity continuous bucket. (*e*) Spaced buckets receive part of lead direct and part by scooping from bottom. (*f*) Continuous: buckets are filled as they pass through loading leg, with feed spout above tail wheel. (*g*) Continuous: buckets in bottomless boot, with cleanout door. (*h*) Malleable-iron spaced buckets for centrifugal discharge. (*i*) Steel buckets for continuous-bucket elevators. (*Stephens-Adamson Division, Allis-Chalmers Corporation.*)

to handle with centrifugal-discharge units. Buckets are closely spaced, with the back of the preceding bucket serving as a discharge chute for the bucket which is dumping as it rounds the head pulley. Close bucket spacing reduces the speed at which the elevator must run to maintain capacities comparable with the spaced-bucket elevator. Gentle discharge prevents excessive degradation and makes this type of elevator effective for handling finely pulverized or aerated materials. Two boot styles and typical loading conditions are illustrated in Fig. 21-5*f* and *g*.

Supercapacity Continuous-Bucket Elevators Elevators of this type (Fig. 21-5*d*) are designed for high lifts and large-lump material. They handle high tonnages and are usually operated at an incline to improve loading and discharge conditions. Operating speeds are low, and because of the heavy loads the bucket-supporting chain is usually guided on the elevating and return runs.

Buckets for spaced-type elevators (Fig. 21-5*h*) are available in both malleable iron and steel in a variety of styles. Style 1 is standard, with style 2 identical except for a reinforced lip. Styles 3 and 4 are low-front designs for wet, stringy, or sticky materials which are difficult to discharge.

Continuous-type buckets (Fig. 21-5*i*) are generally back-mounted to chain or belt at close intervals. They are usually fabricated of steel. Style 5 is standard for normal materials, with style 6 a low-front type for better discharge of difficult materials. Style 7 buckets are used for additional capacity or large lumps, and style 8 for inclined crusher-type elevators. Style 9 buckets are designed for extremely high capacities and are usually side-mounted and hinged together.

Bucket-elevator horsepower can be calculated quite easily. For spaced buckets and digging boots it is equal to the desired capacity in tons per hour multiplied by the lift in feet and divided by 500. For continuous buckets with loading leg, the divisor is increased to 550. Both formulas include normal drive losses as well as loading pickup losses and are applicable for vertical and slightly inclined lifts. For estimating purposes, general bucket-elevator specifications are given for centrifugal units in Table 21-8 and for continuous units in Table 21-9.

V-Bucket Elevator-Conveyors These are still used for handling heavy materials, for coal, and, in light-duty designs, for lightweight free-flowing materials. Similar to the V-bucket type, but with buckets swinging freely on supporting shafts mounted between two strands of roller chain, is the pivoted-bucket conveyor. This type can be equipped with a fixed or movable tripper to dump buckets by overturning them. While considerably more expensive than the V-bucket conveyor, it eliminates the abrasion created by dragging material along in a trough and operates more smoothly at lower power per ton for heavy materials.

The most common chain conveyor is the bucket elevator already discussed, but there are a wide variety of special chain conveyors which are used so infrequently that they should be selected only on the specific recommendation of a qualified materials-handling engineer.

Skip Hoists These hoists, which operate on a batch rather than continuous principle, are not so widely used as in the past. However, for high lifts and extremely lumpy or hot materials, the skip hoist is still an economical and practical device.

Skip hoists may be designed to operate automatically or from a manual push-button station. They are usually classified as uncounterweighted, counterweighted, or balanced. Both the latter systems reduce operating-power requirements, and the balanced unit, using two buckets, can operate at twice the capacity of the others. Figure 21-6 illustrates these types as well as some of the common paths of travel which skip hoists may follow. Speed of operation is also a basis for skip-hoist classification, with multispeed motors required on high-speed operations to slow down bucket travel speed at loading and discharge points.

VIBRATING OR OSCILLATING CONVEYORS

Most vibrating conveyors are essentially directional-throw units which consist of a spring-supported horizontal pan vibrated by a direct-connected eccentric arm, rotating eccentric weights, an electromagnet, or a pneumatic or hydraulic cylinder. The motion imparted to the material particles may vary, but its purpose is to throw the material upward and forward so that it will travel along the conveyor path in a series of short hops.

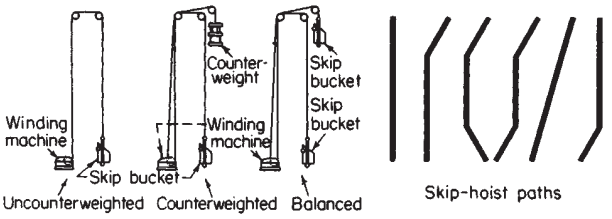


FIG. 21-6 Types of skip hoists and skip-hoist paths. (*Fairfield Engineering Co.*)

The **capacity** of directional-throw vibrating conveyors is determined by the magnitude of trough displacement, frequency of this displacement, angle of throw, slope of trough, and ability of the material to receive and transmit through its mass the directional throw of the trough. The material itself is the most important factor. To be conveyed properly it should have a high friction factor on steel as well as a high internal friction factor so that conveying action is transmitted through its entire depth. Thus deep loads tend to move more slowly than thin ones. Material must also be dense enough to minimize the effect of air resistance on its trajectory, and it should not aerate. Tests have shown that granular materials handle better than pulverized materials and flat or irregular shapes better than spherical ones.

Classification of vibrating conveyors can probably best be based on drive characteristics as shown in Fig. 21-7. All these types transmit vibration to their supporting structures, but the direct, or positive, drive is the worst offender and should be mounted on a heavy supporting structure if it is not counterbalanced. Semipositive- and non-positive-drive types reduce vibration effects because thrust is transmitted over the entire support length rather than at a specific point. Regardless of drive type, care should be taken to mount the conveyor properly so that supporting structures will not be damaged. The frequency of vibration of the conveyor should in no case be at or near the natural frequency of the supporting structure.

Mechanical vibrating conveyors are designed to operate at specific frequencies and do not perform well at other frequencies without carefully designed alterations. Thus they are not adapted to frequent capacity changes except by varying the depth of material fed to the trough. Positive eccentric drives maintain their frequency and magnitude of stroke regardless of load, and serious drive damage can result from overloading. Rotating eccentric weights can also provide the motive force, and although they maintain a constant frequency, the magnitude of stroke is definitely affected by the load. Directional-throw mechanical vibrating conveyors are used primarily for conveying and do not usually perform well as feeders.

Electrical vibrating conveyors are characterized by the fact that there is no contact between the drive and the conveying medium. They operate on a pull-release cycle or a pull-push cycle, using direct current and pulsating electromagnets or alternating current combined with electromagnets and permanent magnets. While most electrical vibrating units are used as feeders, they also work well as conveyors. Most of them offer the advantage of capacity regulation through control of the electric current magnitude via rheostats. Figure 21-8 gives capacities as a function of pan size and power consumption.

Pneumatic and **hydraulic vibrating conveyors** have as their greatest asset elimination of explosion hazards. If pressurized air, water, or oil is available, they can be extremely practical since their drive design is relatively simple and pressure-control valves can be used to vary capacity either manually or automatically.

The **capacity** of vibrating conveyors is extremely broad, ranging from thousands of tons down to grams or ounces. Since so many variables affect their ability to convey, there is no simple formula for figuring capacity and power. Available data are generally the results of

TABLE 21-8 Bucket-Elevator Specifications for Centrifugal-Discharge Buckets on Belt, Malleable-Iron, or Steel Buckets*

Size of bucket, in (mm), and bucket spacing, in (mm)†	Elevator centers, ft‡	Capacity, tons/h (metric tons/h)§	Size of lumps handled, in (mm)¶	Bucket Bucket speed, ft/min (m/min)	r/min, head shaft	hp required at head shaft	Additional hp/ft for intermediate lengths	Head	Tail	Head	Tail	Belt width, in
6 × 4 × 4¼ – 12	25	14 (12.7)	¾ (19.0)	225 (68.6)	43	1.0	0.02	1 15/16	1 1/16	20	14	7
	50	14 (12.7)	¾ (19.0)	225 (68.6)	43	1.6	0.02	1 15/16	1 1/16	20	14	7
(152 × 102 × 108) – (305)	75	14 (12.7)	¾ (19.0)	225 (68.6)	43	2.1	0.02	1 15/16	1 1/16	20	14	7
8 × 5 × 5½ – 14	25	27 (24.5)	1 (25.4)	225 (68.6)	43	1.6	0.04	1 15/16	1 1/16	20	14	9
	50	30 (27.2)	1 (25.4)	260 (79.2)	41	3.5	0.05	1 15/16	1 1/16	24	14	9
(203 × 127 × 140) – (356)	75	30 (27.2)	1 (25.4)	260 (79.2)	41	4.8	0.05	2 7/16	1 1/16	24	14	9
10 × 6 × 6¼ – 16	25	45 (40.8)	1¼ (32.0)	225 (68.6)	43	3.0	0.063	1 15/16	1 15/16	20	16	11
	50	52 (47.2)	1¼ (32.0)	260 (79.2)	41	5.2	0.07	2 7/16	1 15/16	24	16	11
(254 × 152 × 159) – (406)	75	52 (47.2)	1¼ (32.0)	260 (79.2)	41	7.2	0.07	2 15/16	1 15/16	24	16	11
12 × 7 × 7¼ – 18	25	75 (68.1)	1½ (38.1)	260 (79.2)	41	4.7	0.1	2 7/16	1 15/16	24	18	13
	50	84 (76.3)	1½ (38.1)	300 (91.4)	38	8.9	0.115	2 15/16	1 15/16	30	18	13
(305 × 178 × 184) – (457)	75	84 (76.3)	1½ (38.1)	300 (91.4)	38	11.7	0.115	3 7/16	2 7/16	30	18	13
14 × 7 × 7¼ – 18	25	100 (90.8)	1¾ (44.5)	300 (91.4)	38	7.3	0.14	2 15/16	2 7/16	30	18	15
	50	100 (90.8)	1¾ (44.5)	300 (91.4)	38	11.0	0.14	3 7/16	2 7/16	30	18	15
(355 × 179 × 184) – (457)	75	100 (90.8)	1¾ (44.5)	300 (91.4)	38	14.3	0.14	3 7/16	2 7/16	30	18	15
16 × 8 × 8½ – 18	25	150 (136.2)	2 (50.8)	300 (91.4)	38	8.5	0.165	2 15/16	2 7/16	30	20	18
	50	150 (136.2)	2 (50.8)	300 (91.4)	38	12.6	0.165	3 7/16	2 7/16	30	20	18
(406 × 203 × 216) – (457)	75	150 (136.2)	2 (50.8)	400 (121.9)	38	16.7	0.165	3 15/16	2 7/16	30	20	18

*From Stephens-Adamson Division, Allis-Chalmers Corporation.

†Bucket size given: width × projection × depth. Assumed bucket linear speed is 150 ft/min (45.7 m/min).

‡Elevator centers to nearest SI equivalent are 25 ft ≃ 8 m, 50 ft ≃ 15 m, and 75 ft ≃ 23 m.

§Capacities and horsepowers are given for materials having bulk densities of 100 lb/ft^3 (1602 kg/m^3). For other densities these will vary in direct proportion: a 50-lb/ft^3 material will reduce the capacity and horsepower required by 50 percent.

¶If the amount of lump product is less than 15 percent of the total, lump size may be twice that given.

TABLE 21-9 Bucket-Elevator Specifications for Continuous Buckets on Chain*

Size of bucket and bucket spacing, in (mm)†	Elevator centers, ft‡	Capacity, tons/h (metric tons/h)§	Size of lumps handled, in (mm)¶	r/min, head shaft	hp required at head shaft	Additional hp/ft for intermediate lengths	Head	Tail	Head	Tail
8 × 5½ × 7¾ – 8	25	35 (31.7)	1 (25.4)	28	1.8	0.06	1 15/16	1 1/16	20½	14
(203 × 140 × 197) – (203)	50	35 (31.7)	1 (25.4)	28	3.4	0.06	2 7/16	1 1/16	20½	14
	75	35 (31.7)	1 (25.4)	28	5.0	0.06	2 15/16	1 1/16	20½	14
10 × 7 × 11¾ – 12	25	60 (54.5)	1½ (38.1)	23	3.0	0.10	2 7/16	1 15/16	25	17½
(254 × 178 × 298 – (305)	50	60 (54.5)	1½ (38.1)	23	5.5	0.10	2 7/16	1 15/16	25	17½
	75	60 (54.5)	1½ (38.1)	23	8.0	0.10	2 15/16	1 15/16	25	17½
12 × 7 × 11¾ – 12	25	70 (63.5)	1½ (38.1)	23	3.5	0.12	2 7/16	1 15/16	25	17½
(305 × 178 × 298) – (305)	50	70 (63.5)	1½ (38.1)	23	6.5	0.12	2 15/16	1 15/16	25	17½
	75	70 (63.5)	1½ (38.1)	23	9.5	0.12	3 7/16	2 7/16	25	17½
14 × 7 × 11¾ – 12	25	80 (72.6)	1¾ (44.5)	23	4.0	0.14	2 7/16	2 7/16	25	17½
(356 × 178 × 298) – (305)	50	80 (72.6)	1¾ (44.5)	20	7.5	0.14	2 15/16	2 7/16	29	17½
	75	80 (72.6)	1¾ (44.5)	20	11	0.14	3 7/16	2 7/16	29	17½
14 × 8 × 11¾ – 12	25	100 (90.8)	2 (50.8)	20	5.0	0.17	2 15/16	2 7/16	29	17½
(356 × 203 × 298) – (305)	50	100 (90.8)	2 (50.8)	20	9.3	0.17	3 7/16	2 7/16	29	17½
	75	100 (90.8)	2 (50.8)	20	13.3	0.17	3 15/16	2 7/16	29	17½
16 × 8 × 11¾ – 12	25	115 (104.4)	2 (50.8)	20	6.0	0.20	2 15/16	2 7/16	29	17½
(406 × 203 × 298) – (305)	50	115 (104.4)	2 (50.8)	20	11	0.20	3 15/16	2 7/16	29	17½
	75	115 (104.4)	2 (50.8)	20	16	0.20	4 7/16	2 7/16	29	17½
18 × 8 × 11¾ – 12	25	130 (118.0)	2 (50.8)	20	7	0.22	2 15/16	2 7/16	29	17½
(406 × 203 × 298) – (305)	50	130 (118.0)	2 (50.8)	20	13	0.22	3 15/16	2 7/16	29	17½
	75	130 (118.0)	2 (50.8)	20	20	0.22	4 7/16	2 7/16	29	17½

*From Stephens-Adamson Division, Allis-Chalmers Corporation.
†Bucket size given: width × projection × depth. Assumed bucket linear speed is 150 ft/min (45.7 m/min).
‡Elevator centers to nearest SI equivalent are 25 ft ≃8 m, 50 ft ≃15 m, and 75 ft ≃23 m.
§Capacities and horsepowers are given for materials having bulk densities of 100 lb/ft^3 (1602 kg/m^3). For other densities these will vary in direct proportion: a 50-lb/ft^3 material will reduce the capacity and horsepower required by 50 percent.
¶If the total amount of lump product is less than 15 percent of the total, lump size may be twice that given.

experiments and empirical equations, with most manufacturers providing selection charts for specific types of conveyors and materials. A typical leaf-spring unit is shown in Fig. 21-8, along with the graphical information required to select a standard unit. Conveyor lengths are limited to about 61 m (200 ft) with multiple drives and about 30.5 m (100 ft) with a single drive. There are many exceptions to these general limitations, and they should not preclude study of a specific problem when vibrating conveyors seem desirable.

Processing operations of many types can be carried out in vibrating conveyors because their simple conveying troughs can be modified quite easily. While tube and flat-pan troughs are most common, troughs can be provided in a wide variety of shapes and materials. Although conveying action is usually so gentle that abrasion problems do not arise, such problems can be easily solved when they do occur by the use of special materials or liners. Troughs are easily sealed to prevent contamination or for operation under positive or negative pressure. With screen or perforated deck plates, vibrating conveyors can dewater, rough-screen, scalp, or dry. Heating and cooling can also be handled by the use of air streams blowing over or through the material, infrared panels, resistance-heating panels, or contact with air- or water-cooled or heated trough casings. Special vibrating-conveyor designs are available for elevating at relatively steep slopes or up a spiral trough. There is probably no other conveyor so readily adaptable to the solution of processing problems.

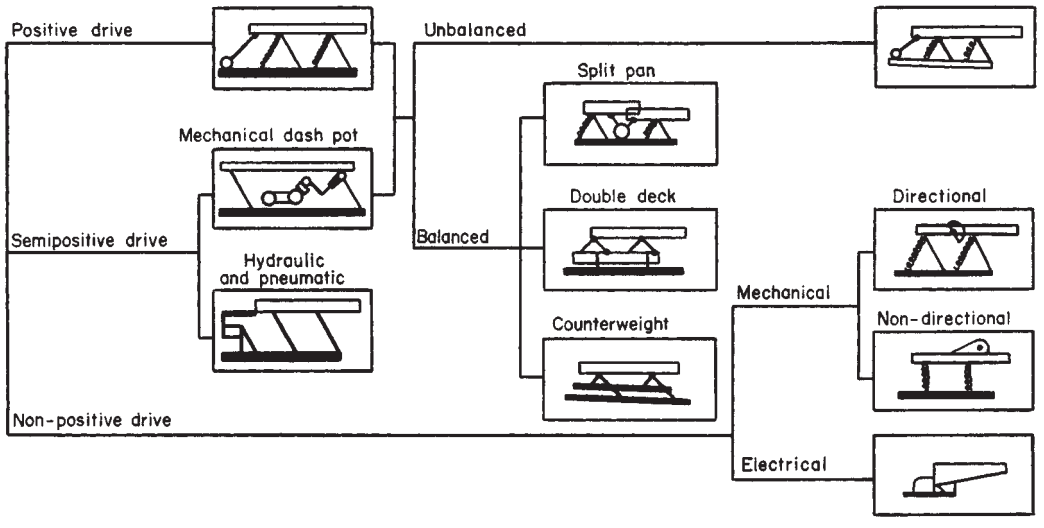
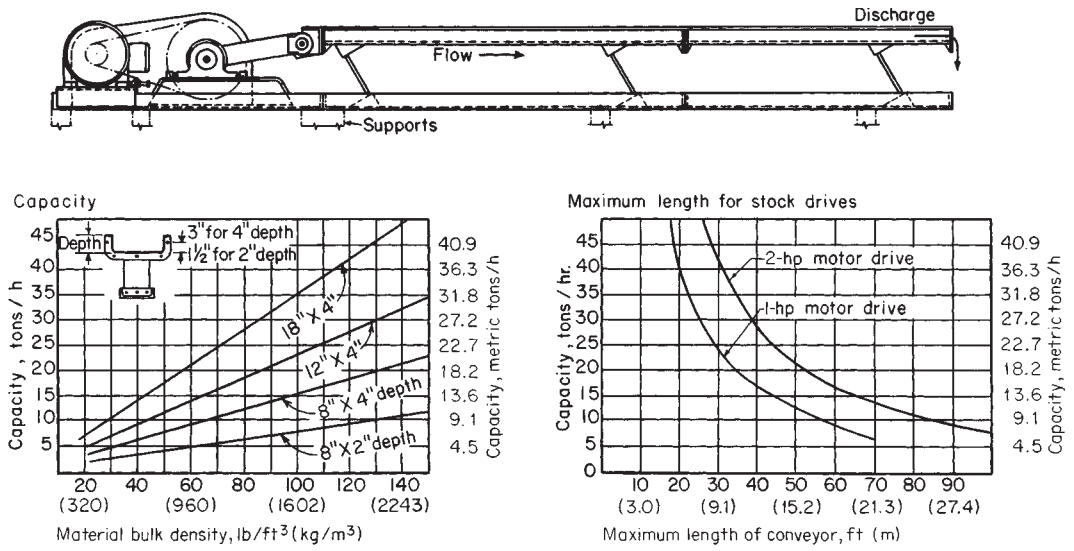


FIG. 21-7 Vibration-conveyor classification. (*Modern Materials Handling.*)



Pan width and stream depth: nearest metric equivalents

in	mm	in	mm
18 x 4	450 x 100	8 x 4	200 x 100
12 x 4	300 x 100	8 x 2	200 x 50

FIG. 21-8 Standardized leaf-spring mechanical oscillating conveyor with selection charts. Multiply pounds per cubic foot by 16.02 to get kilograms per cubic meter; multiply feet by 0.3048 to get meters. (*FMC Corporation, Materials Handling Systems Division.*)

CONTINUOUS-FLOW CONVEYORS

The principle of the continuous-flow conveyor is that when a surface is pulled transversely through a mass of granular, powdered, or small-lump material, it will pull along with it a cross section of material which is greater than the area of the surface itself. The conveying action of various designs of continuous-flow conveyors varies with the type of conveying flight but theoretically is not comparable with the action in a flight or drag conveyor. Flights vary from solid surfaces to skeleton designs, as shown in Fig. 21-9.

The continuous-flow conveyor is a totally enclosed unit which has a relatively high capacity per unit of cross-sectional area and can follow an irregular path in a single plane. These features make it extremely versatile. Figure 21-10 shows some typical arrangements and applications possible with these conveyors. Included is an example of the unit acting as a dewatering device (Fig. 21-10*c*).

These conveyors employ a chain-supported conveying element (some are cast integrally with the chain, which is designed with easily detachable knuckle joints). Thus the connecting element runs along the outside of the casing so that head and tail sections do not become excessively large because of projecting conveying elements. This means that the material feeding into the conveyor must fall past the chain element and travel in a reverse direction before passing into the actual conveying leg (see Fig. 21-10*c*). Since this affects the lump size that the conveyor can conveniently handle, the loop design (Fig. 21-10*c*) is sometimes used for better feeding conditions, or separate carrying runs and return runs are provided with inclined loading chutes to the lower carrying run. In any event, lump size and abrasive

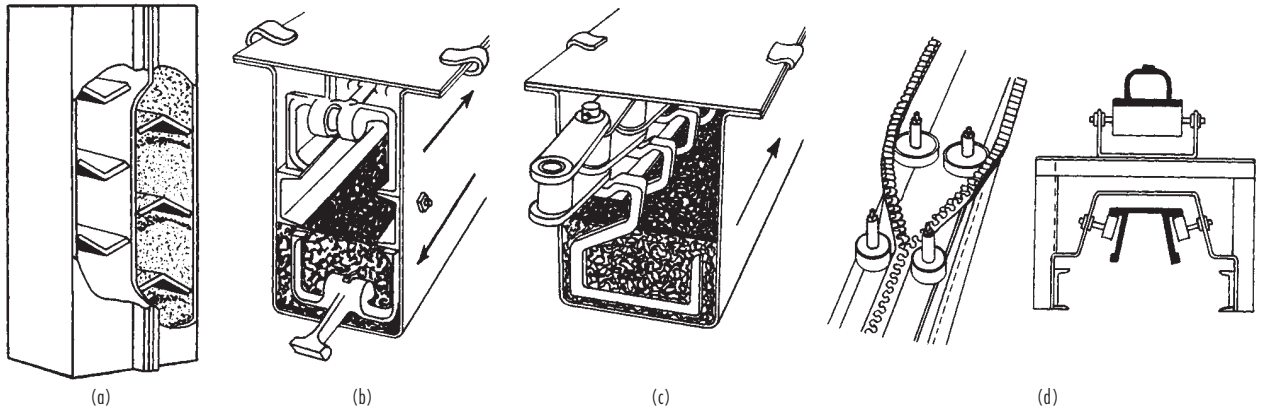


FIG. 21-9 Closed and open flights for continuous-flow conveyors. (*a*) and (*b*) Conveyor-elevator. (*c*) Horizontal conveyor with side-pull chain. (*d*) Detail of closed-belt conveyor; opening and closing rollers mesh and unmesh teeth in the same manner as a conventional clothing fastener. (*FMC Corporation, Material Handling Systems Division; Stephens-Adamson Division, Allis-Chalmers Corporation.*)

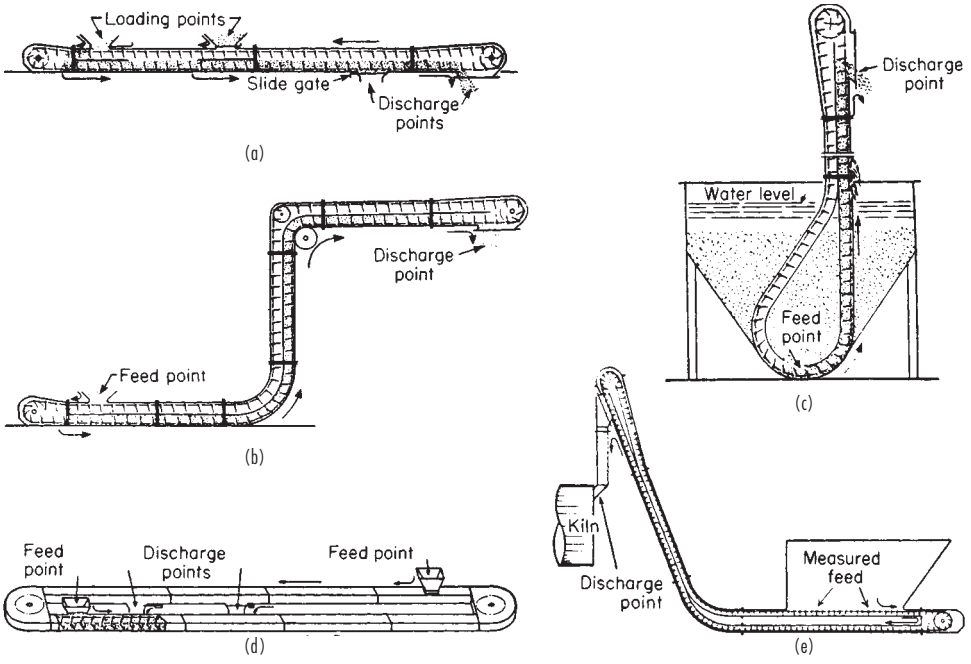


FIG. 21-10 Typical arrangements and applications for continuous-flow conveyors. (*a*) Horizontal conveyor. (*b*) Z-type conveyor-elevator. (*c*) Loop-feed elevator used for dewatering. (*d*) Side-pull horizontal recirculating conveyor. (*e*) Horizontal inclined conveyor-elevator. (*Stephens-Adamson Division, Allis-Chalmers Corporation.*)

characteristics of material are important considerations in the selection of continuous-flow conveyors.

The side-pull continuous-flow conveyor can follow a variety of paths in a horizontal plane, picking up and discharging material at many different points. Figure 21-9*c* is a detailed illustration of one type of conveying element, and Fig. 21-10*d* shows a typical arrangement with 180° turns. Triangular arrangements and rectangular layouts with 90° corners are also available.

The **capacity** of the continuous-flow conveyor is dependent on the particular design being considered. Limiting speeds are subject to considerable controversy. It is advisable to follow the manufacturer's recommendations closely for best conveyor service. **Power** calculations depend on a number of experimentally determined constants which vary for different conveyor designs. One factor contributing to total power requirements is the power required on bend corners where flights assume a radial position and tend to compress material which was fed between them when they were running in a parallel position. Noncompressible materials may require special clearances and feed conditions. Thus, while conveyor components have been well standardized, many materials will not convey well unless special design alterations are made.

Because of the fabrication required for casings and the precision fitting of conveying elements within it, the continuous-flow conveyor is normally an expensive unit. However, it occupies little space, needs little support because the casing forms a rigid box girder, may travel in several directions with only a single drive, is self-feeding, and can feed and discharge at several points. These factors may often compensate for what sometimes appears as a rather high cost per foot. Because it is adaptable to many processing operations, the continuous-flow conveyor is widely used in the chemical industry, in which there is a great deal of rehandling or requirements for many feed and discharge points. The conveyors can be designed for self-cleaning to allow different materials to be handled in the same unit without contamination.

Closed-Belt Conveyor This device, with zipperlike teeth which mesh to form a closed tube, is particularly adaptable to the problem of handling fragile materials which cannot be subjected to degradation. Since the belt is wrapped snugly around the material, it moves with the belt and is not subject to any form of internal movement except at feed and discharge. In addition, the belt can operate in many planes, with twists and turns to meet almost any layout condition within the fixed limit of curvature placed on the loaded belt. It can convey and elevate with only a single drive; multiple feed and discharge points are relatively easy to arrange.

The closed-belt conveyor is not readily adaptable to the handling of sticky materials, and special designs may be required for materials which are highly susceptible to aeration. Initial cost per foot is relatively high because of belting cost, but power requirements are low and with proper installation and maintenance belt life is good.

Since this type of conveyor is available in only one standard size, its capacity is determined by the belt speed and the fixed cross-sectional area. Tons-per-hour capacity is figured by multiplying the bulk density in pounds per cubic foot by the speed in feet per minute and a constant of 0.0021. Power requirements are quite low and figured in the same way as those for conventional belt conveyors.

Figure 21-9*d* illustrates a typical closed-belt-conveyor detail of the opening or closing mechanism and a cross section through a horizontal carrying-and-return run. Designs using two conventional conveyor belts have been developed to elevate material by pressing it between them, but their application is limited.

Flight Conveyors These devices are available in an almost infinite variety. Most flight-conveyor applications are open designs for rough conveying operations, but some are built with totally enclosed easings. Table 21-10 gives typical design and capacity information.

Apron Conveyors Probably the most common chain conveyors, these are available in a wide variety of designs for both horizontal and inclined travel. Their main application is the feeding of material at controlled rates, with lump sizes that are large enough to minimize dribble. The typical design is a series of pans mounted between two strands of roller chain, with pans overlapping to eliminate dribble, and often equipped with end plates for deeper loads. Pan design may vary according to material requirements. Figure 21-11 illustrates a typical apron-conveyor design, and Table 21-11 gives capacities for units with and without skirt plates. Apron-feeder applications range from fairly

TABLE 21-10 Flight-Conveyor Capacities*

Flight size and no. of strands, in (mm)	Maximum size of lumps: All lumps, in (mm)	Maximum size of lumps: 10% lumps, in (mm)	Capacity, tons/h (metric tons/h)† for various flight spacings, conveyor, horizontal, in (mm): 18 (460)	24 (610)	36 (915)	Design type‡
10 × 4 (255 × 100)—1	1½ (38)	3 (76)	32 (29)	25 (23)	16 (15)	1
12 × 5 (305 × 130)—1	1¾ (45)	3½ (89)	46 (42)	35 (32)	23 (21)	1
15 × 5 (380 × 130)—1	2 (51)	4 (102)	66 (60)	50 (45)	33 (30)	1
15 × 6 (380 × 155)—2	3½ (89)	7 (178)	87 (79)	67 (61)	44 (40)	2
16 × 8 (405 × 205)—2	4 (102)	8 (203)	110 (99)	82 (74)	55 (50)	2
18 × 8 (460 × 205)—2	5 (127)	9 (229)	124 (113)	93 (84)	62 (56)	2
20 × 10 (510 × 255)—2	6 (152)	10 (254)	— —	141 (128)	94 (85)	2
24 × 10 (610 × 255)—2	8 (203)	13 (305)	— —	176 (160)	116 (105)	2
30 × 10 (765 × 255)—2	10 (254)	14 (355)	— —	— —	250 (227)	2
12 × 5 (305 × 130)—1	1¾ (45)	3½ (89)	56 (51)	42 (38)	28 (25)	3
15 × 7 (380 × 180)—1	2½ (64)	4½ (114)	78 (71)	58 (53)	39 (35)	3
18 × 8 (460 × 205)—1	3 (76)	5 (127)	124 (113)	93 (84)	62 (56)	3
12 × 5 (305 × 130)—2	2 (51)	4 (102)	56 (51)	4 (38)	28 (25)	4
15 × 6 (380 × 155)—2	3 (76)	5 (127)	76 (69)	57 (52)	38 (34)	4
18 × 7 (460 × 180)—2	4 (102)	8 (203)	96 (87)	72 (65)	48 (44)	4
24 × 8 (610 × 205)—2	8 (203)	12 (305)	— —	124 (113)	83 (75)	4

*Data from Fairfield Engineering Co.
†Basis: 30-lb/ft³ (480-kg/m³) bulk density and conveyor velocity of 100 ft/min (30.5 m/min). For inclined conveyors capacities are reduced by factors given:

Slope off horizontal	Factor
15°	0.80
30°	0.55
45°	0.33

‡Type 1: malleable-iron conveyor flights; type 2: steel flights on roller chain; type 3: steel flights with wear shoes or rollers; type 4: steel flights on plain chain.

light-duty applications with light-gauge steel pans up to extremely heavy-duty applications requiring reinforced manganese steel pans with center supports. Table 21-11 values may be used in calculating capacities of other sizes, since this is a function of width of carrying surface, height of sides, speed, and bulk density. Apron-conveyor speeds are typically 0.25 to 0.38 m/s (50 to 75 ft/min). When these conveyors are used as feeders, velocities are kept in the 0.05- to 0.15-m/s (10- to 30-ft/min) range.

PNEUMATIC CONVEYORS

One of the most important material-handling techniques in the chemical industry is the movement of material suspended in a stream of air over horizontal and vertical distances ranging from a few to several hundred feet. Materials ranging from fine powders through 6.35-mm (¼-in) pellets and bulk densities of 16 to more than 3200 kg/m³ (1 to more than 200 lb/ft³) can be handled. A large, capable manufacturing

TABLE 21-11 Apron-Conveyor Capacities*

Capacity without skirts for various speeds and bulk densities for material depth of 4 in (102 mm) on pans

Apron width, in (mm)	50 ft/min (15.2 m/min): ft³/h (m³/h)	tons/h: 50 lb/ft³ (801 kg/m³)	(metric tons/h): 100 lb/ft³ (1602 kg/m³)	100 ft/min (30.5 m/min): ft³/h (m³/h)	ton/h: 50 lb/ft³ (801 kg/m³)	(metric tons/h): 100 lb/ft³ (1602 kg/m³)
18 (460)	1125 (31.9)	28 (25)	56 (51)	2250 (63.7)	56 (51)	112 (102)
24 (610)	1500 (42.5)	38 (34)	75 (68)	3000 (85.0)	75 (68)	150 (136)
30 (765)	1875 (53.2)	47 (43)	94 (85)	3750 (106.2)	94 (85)	188 (171)
36 (915)	2250 (63.7)	56 (51)	113 (102)	4500 (127.4)	113 (102)	226 (205)
42 (1070)	2625 (74.3)	66 (60)	131 (119)	5250 (148.7)	131 (119)	262 (238)
48 (1220)	3000 (85.0)	75 (68)	150 (136)	6000 (170.0)	150 (136)	300 (272)
54 (1370)	3375 (95.6)	85 (77)	169 (153)	6750 (191.2)	169 (153)	338 (307)
60 (1525)	3750 (106.2)	94 (85)	188 (171)	7500 (212.4)	188 (171)	376 (341)

Capacities with skirts for various material depths, 0.75 loaded cross section and 10-ft/min (3-m/min) velocity

Pan width, in (mm)	Width between skirts, in (mm)	Max: lump size, in (mm)	Capacity, tons/h (metric tons/h); 50-lb/ft³ (801-kg/m³) bulk-density material; material depth on pans, in (mm): 4 (105)	8 (205)	12 (305)	18 (460)	21 (535)	24 (610)
18 (460)	16 (410)	3 (76)	5.0 (4.5)	10.0 (9.1)	15.0 (13.6)	22.5 (20.4)	26.3 (23.9)	30.0 (27.2)
24 (610)	22 (560)	4 (102)	6.9 (6.3)	13.7 (12.4)	20.6 (18.7)	31.0 (28.1)	36.1 (32.8)	41.2 (37.4)
30 (765)	28 (715)	6 (152)	8.8 (8.0)	17.5 (15.9)	26.2 (23.8)	39.3 (35.7)	45.9 (41.7)	52.5 (47.7)
36 (915)	34 (865)	8 (203)	10.7 (9.7)	21.3 (19.3)	32.0 (29.1)	48.0 (43.6)	56.0 (51.8)	64.0 (58.1)
42 (1070)	40 (1020)	10 (254)	12.5 (11.3)	25.0 (22.7)	37.5 (34.0)	56.3 (51.1)	65.7 (59.6)	75.0 (68.1)
48 (1220)	46 (1170)	12 (305)	14.4 (13.1)	28.8 (26.1)	43.2 (39.2)	64.8 (58.8)	75.6 (68.6)	86.3 (78.3)

*Data from Fairfield Engineering Co.

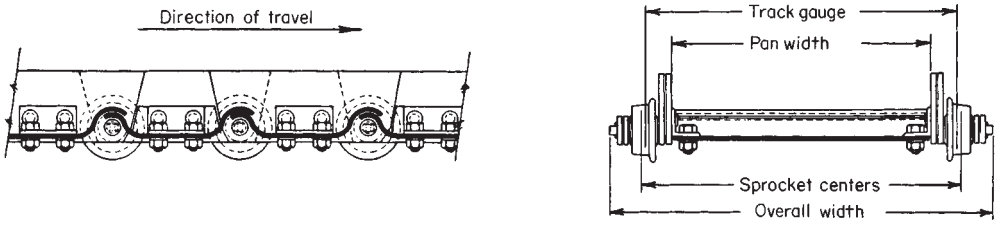


FIG. 21-11 Apron conveyors. (*Fairfield Engineering Co.*)

industry supplies complete systems as well as components that users can incorporate into their own designs. Much engineering information is available from this industry in the form of brochures, data sheets, and nomographs.

The **capacity** of a pneumatic-conveying system depends on (1) product bulk density (and particle size and shape to some extent), (2) energy content of the conveying air over the entire system, (3) diameter of conveying line, and (4) equivalent length of conveying line.

Minimum capacity is achieved when the energy of the conveying air is just sufficient to move the product through the line without stoppage. To prevent such stoppage, it is good practice to provide an additional increment of air energy so that a factor of safety exists that allows for minor changes in product characteristics. An **optimum system** is one that repays, through operating economies, all design features above the minimum required, within the return-on-investment criteria set by the owner.

While successful and economical system designs can be devised by experienced process engineers, the competent technical aid available from equipment suppliers has led to a growing trend toward the purchase of complete systems, even on small jobs, rather than in-plant assembly from components on the basis of in-house designs. An idea of the change in **capital investment** for typical pneumatic-conveyor systems as a function of increasing transfer rates is given in Table 21-12.

Conveyor installations may be permanent or a combination of permanent and portable. The latter kind is often mounted on a bulk-delivery vehicle, which permits fast unloading into the customer's silo by the carrier without effort or equipment from the customer. Controls range from simple motor starters and hand-connected hoses to sophisticated, microprocessor-electropneumatic control systems.

Types of Systems Generally, pneumatic conveyors are classified according to five basic types: pressure, vacuum, combination pressure and vacuum, fluidizing, and the blow tank.

In **pressure systems** (Fig. 21-12*a*), material is dropped into an air stream (at above atmospheric pressure) by a rotary air-lock feeder. The velocity of the stream maintains the bulk material in suspension until it reaches the receiving vessel, where it is separated from the air by means of an air filter or cyclone separator.

Pressure systems are used for free-flowing materials of almost any particle size, up to 6.35-mm (¼-in) pellets, where flow rates over 151 kg/min (20,000 lb/h) are needed and where pressure loss through the system is about 305 mmHg (12 inHg). These systems are favored when one source must supply several receivers. Conveying air is usually supplied by positive-displacement blowers.

Vacuum systems (Fig. 21-12*b*) are characterized by material moving in an air stream of pressure less than ambient. The advantages of this type are that all the pumping energy is used to move the product and that material can be sucked into the conveyor line without the need of a rotary feeder or similar seal between the storage vessel and the conveyor. Material remains suspended in the air stream until it reaches a receiver. Here, a cyclone separator or filter (Fig. 21-12*c*) separates the material from the air, the air passing through the separator and into the suction side of the positive-displacement blower or some other power source.

Vacuum systems are typically used when flows do not exceed 6800 kg/h (15,000 lb/h), the equivalent conveyor length is less than 305 m (1000 ft), and several points are to be supplied from one source. They are widely used for finely divided materials. Of special interest are vacuum systems designed for flows under 7.6 kg/min (1000 lb/h), used to transfer materials short distances from storage bins or bulk containers to process units. This type of conveyor is widely used in plastics and other processing operations where the variety of conditions requires flexibility in choosing pickup devices, power sources, and receivers. Capital investment can be kept low, often in the range of $2000 to $7000.

Pressure-vacuum systems (Fig. 21-12*c*) combine the best of both the pressure and the vacuum methods. A vacuum is used to induce material into the conveyor and move it a short distance to a separator. Air passes through a filter and into the suction side of a positive-displacement blower. Material then is fed by a rotary feeder into the conveyor positive-pressure air stream, which comes from the blower discharge. Application can be very flexible, ranging from a central control station, with all interconnection activities electrically controlled and sequenced, to one in which activities are handled by manually changing conveyor connections. The most typical application is the combined bulk vehicle unloading and transferring to product storage (Fig. 21-12*d*).

Fluidizing systems generally convey prefluidized, finely divided, non-free-flowing materials over short distances, such as from storage bins or transportation vehicles to the entrance of a main conveying

TABLE 21-12 Approximate Pneumatic-Conveyor Costs*

Flow rate, lb/h	(kg/h)	Conveyor pipe, inside diameter, in	(mm)	Power required, hp	Range of investment, $† Manual‡	Automatic§
10,000	(4,536)	4	(100)	25	83,000	46,000
25,000	(11,340)	6	(155)	60	135,000	89,000
50,000	(22,680)	6	(155)	125	200,000	155,000
100,000	(45,360)	8	(205)	200	356,000	312,000

*Product: Plastic pellets, ⅛-in (3.2-mm) cubes, 30-lb/ft^3 (481-kg/m^3) bulk density; equivalent length of system, 600 ft (183 m)

†1995 costs. Equipment includes motor and blower package, cyclone receivers, railcar-unloading connections, high-level interlocks for stopping the motor and blower combination when the silos reach a full level, and all necessary piping. Installation is not included.

‡System includes a minimum control package, with most activities person-actuated, including the changing of feed lines to storage silos.

§System includes automatic actuation of most activities, with changing of feed lines to silos accomplished by diverter valves controlled automatically by process control computer.

system. A particular advantage in storage-bin applications is that the bottom of the bin is permitted to be nearly horizontal. Fluidizing is accomplished by means of a chamber in which air is passed through a porous membrane that forms the bottom of the conveyor, upon which the material to be conveyed rests. As air passes through the membrane, each particle is surrounded by a film of air (Fig. 21-12*e*). At the point of incipient fluidization the material takes on the characteristics of free flow. It can then be passed into a conveyor air stream by a rotary feeder.

Prefluidizing has the advantage of reducing the volume of conveying air needed; consequently, less power is required. The characteristics of the rest of this system are similar to those of regular pressure- or vacuum-type conveyors. Of special concern is the tendency of material to stick to and build up on surfaces of the system components. The most common application of this type of conveyor is the well-known railroad Airslide covered hopper car.

An early application of pneumatic conveying was the **blow tank.** This device functions by introducing pressurized air on top of a head of material contained in a pressure vessel. If the material is free-flowing, it will flow through a valve at the bottom of the chamber and move through a short conveying line, usually limited to a maximum of 16 m (50 ft), depending on the product, although systems as long as 457 m (1500 ft) are in use. Of special concern when using this system are the surges of air caused either by the tank emptying or by the air breaking through the product.

The blow-tank principle can be used to feed regular pneumatic conveyors. Use of an Airslide or other fluidizing device at the bottom of the blow tank permits handling non-free-flowing materials. This

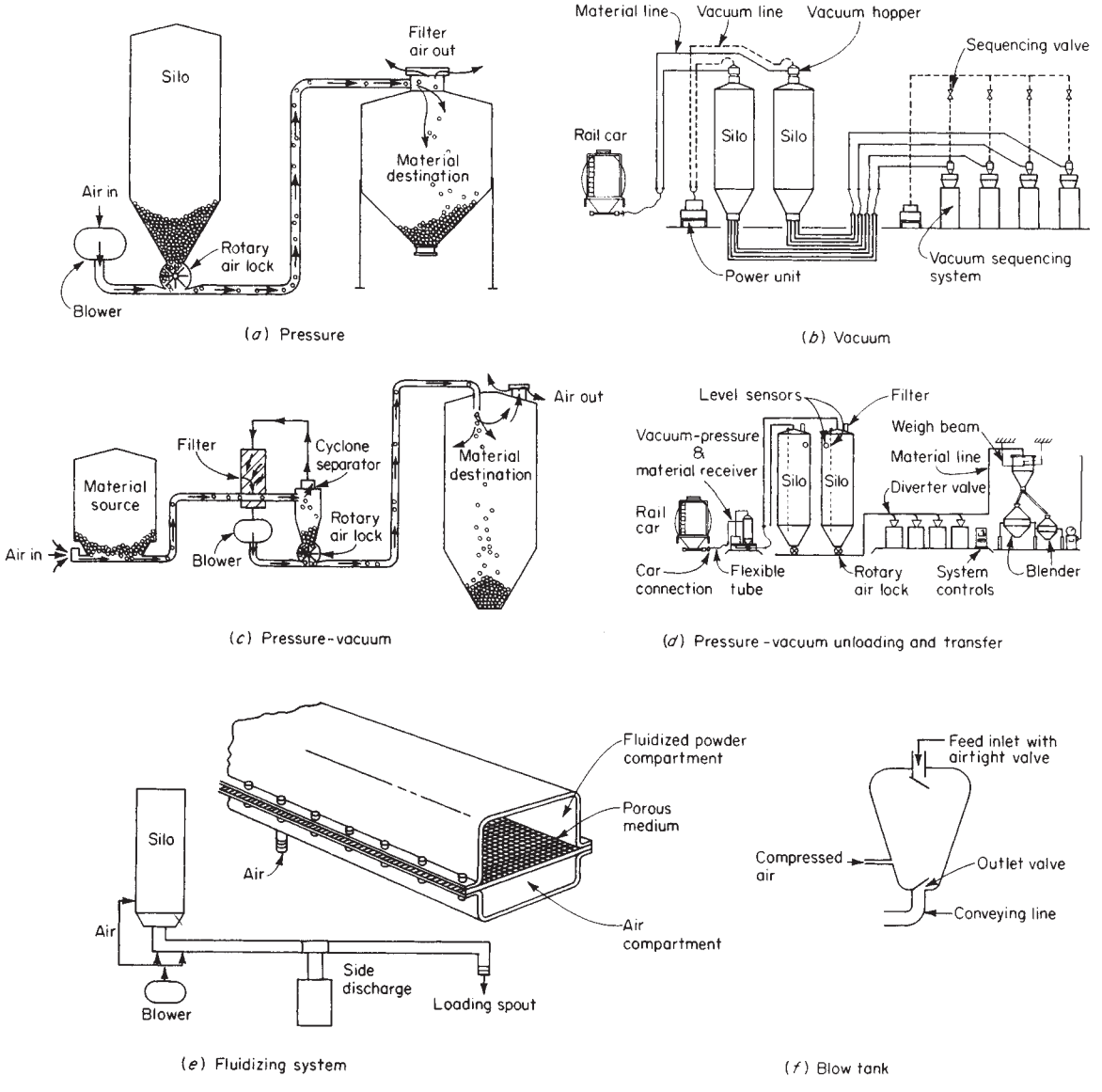


FIG. 21-12 Types of air-conveying systems. (*a*) Pressure. (*b*) Vacuum. (*c*) Pressure-vacuum. (*d*) Pressure vacuum unloading and transfer. (*Whitlock, Inc.*) (*e*) Fluidizing system. (*Fuller Co.*) (*f*) Blow tank.

principle is used extensively in pressure-fluidizing-type valve-bag-packing machines.

Nomographs for Preliminary Design A useful set of nomographs* for determining conveyor-design parameters is given in Fig. 21-13. With these charts, conservative approximations of conveyor size and power for given product bulk density, conveyor equivalent length, and required capacity can be obtained. Because pneumatic conveyors and their components are subject to continual improvements by a fast-changing supplier industry, manufacturers should be invited to submit alternative designs to that resulting from the use of the nomograph. Some large users of pneumatic conveyors have found it expedient to write computer programs for calculating system parameters.

* Nomographs prepared from data supplied by Flotronics Division, Allied Industries.

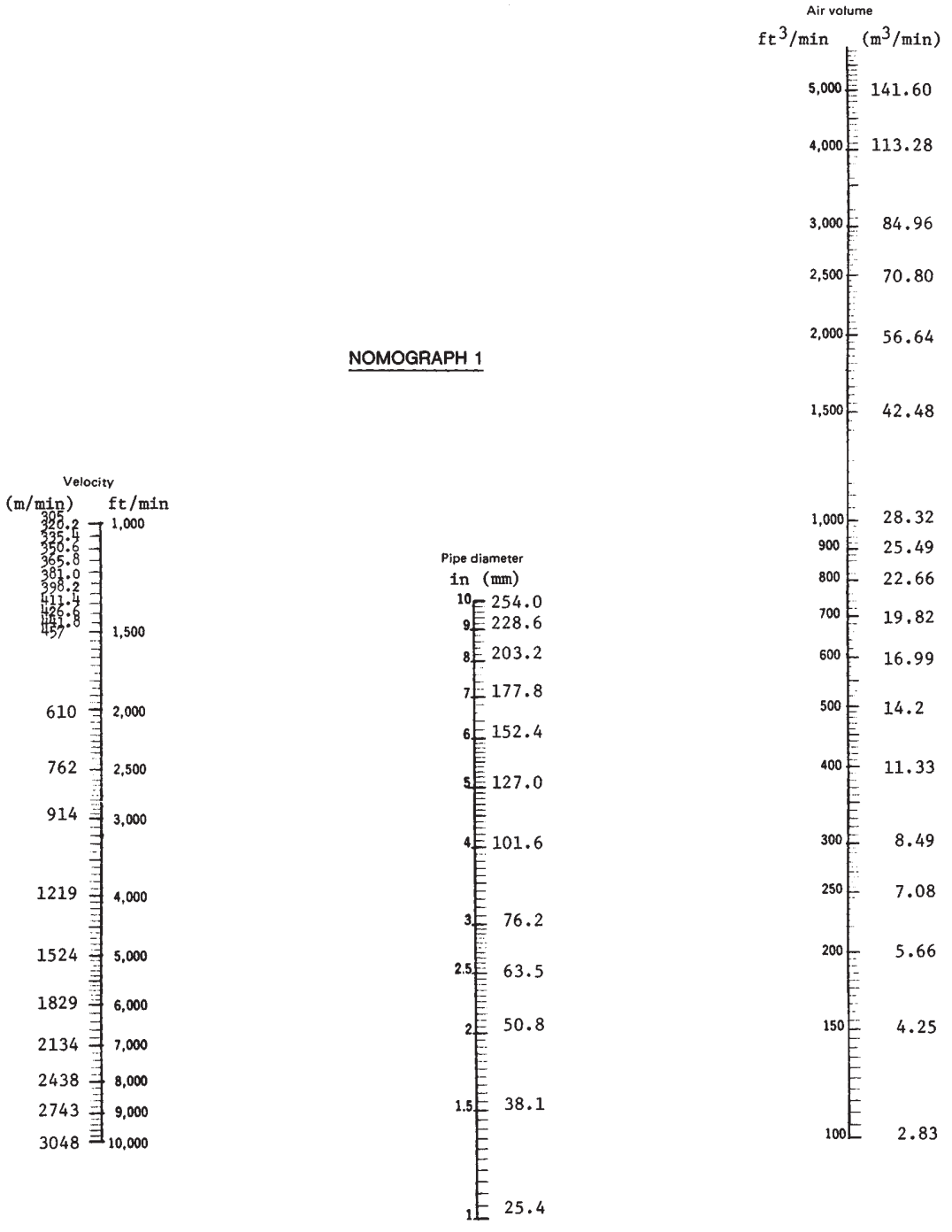


FIG. 21-13 Nomographs for determining conveyor-design parameters.

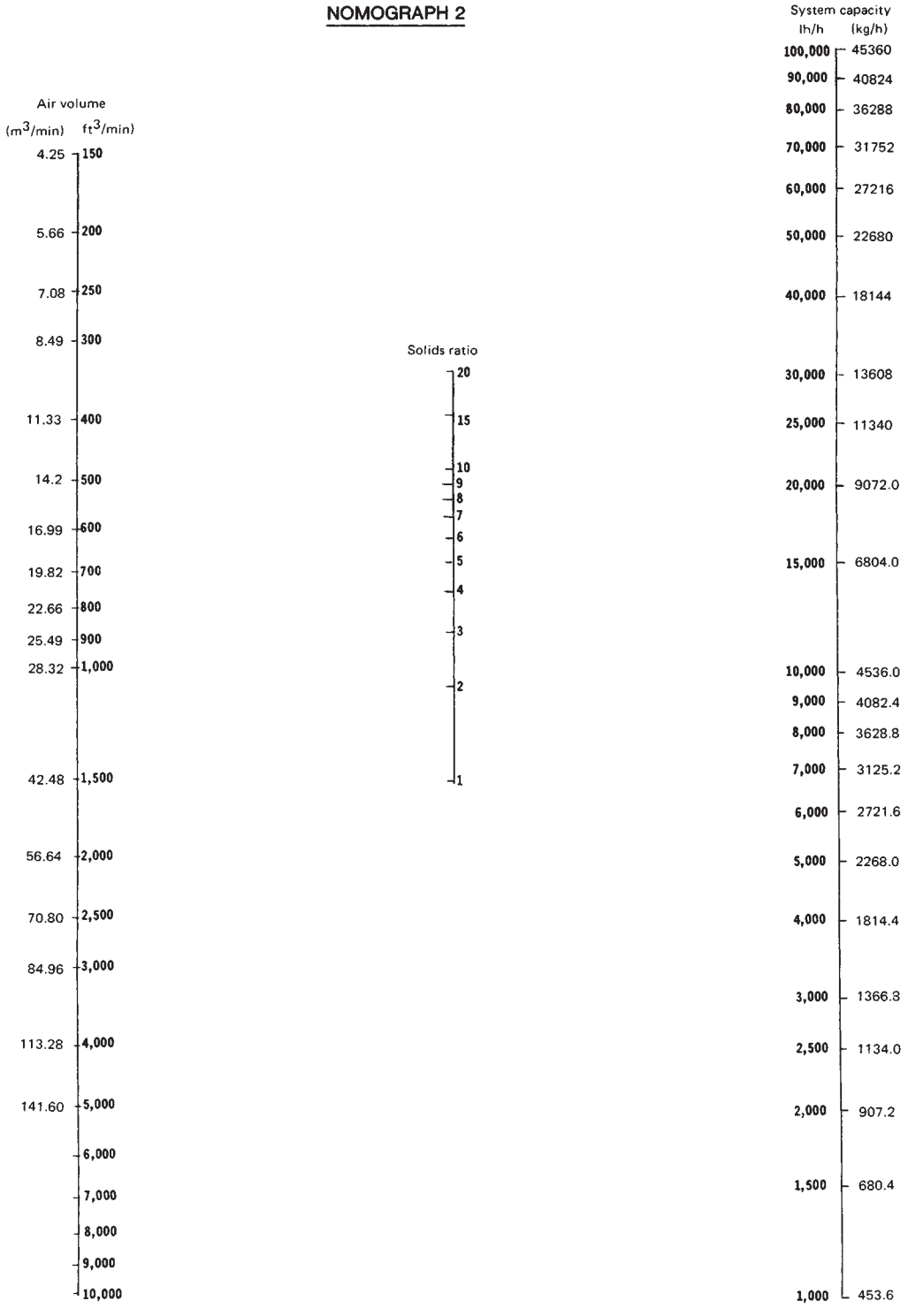


FIG. 21-13 (*Continued*)

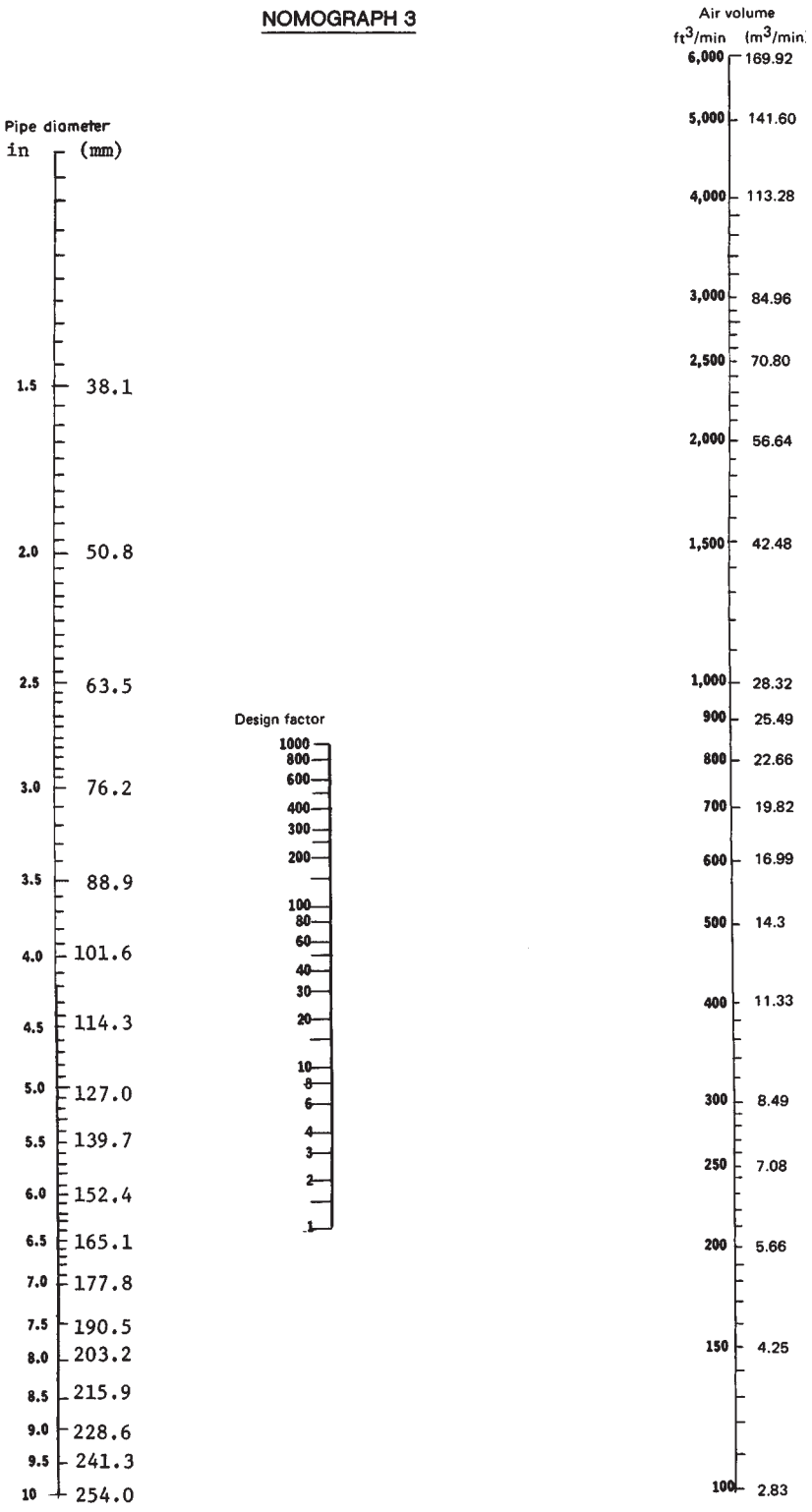


FIG. 21-13 (*Continued*)

NOMOGRAPH 4

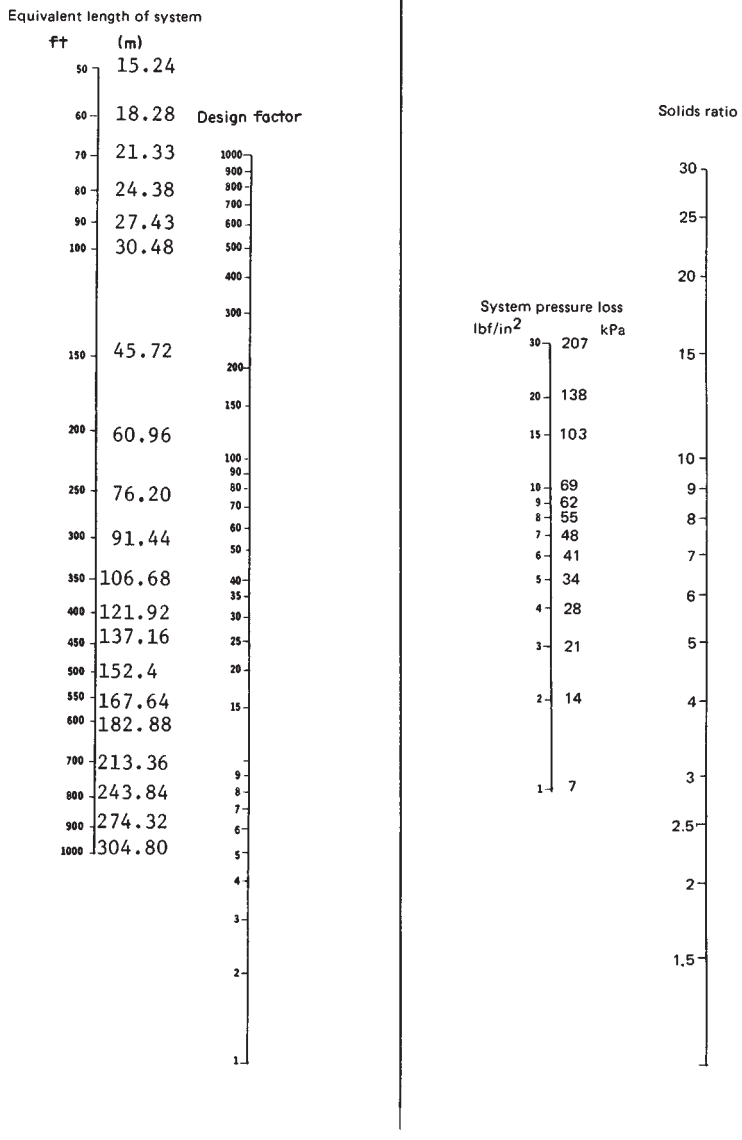


FIG. 21-13 (*Continued*)

To begin preliminary calculations, first determine the equivalent length of the system being considered. This length is the sum of the vertical and horizontal distances, plus an allowance for the pipe fittings used. Most common of these fittings are the long-radius 90° elbow pipe [equivalent length = 25 ft (7.6 m)] and the 45° elbow [equivalent length = 15 ft (4.6 m)].

The second step consists of choosing from Table 21-13 an initial air velocity that will move the product. An iterative procedure then begins by assuming a pipe diameter for the required capacity of the system.

Referring now to Nomograph 1, draw a straight line between the air-velocity and the pipe-diameter scales so that when the line is extended it will intersect the air-volume scale at a certain point.

Turn now to Nomograph 2 and locate in their respective scales the air volume and the calculated system capacity. A straight line between these two points intersects the scale in between them, thus providing at the intersection point the value of the solids ratio. If the solids ratio exceeds 15, assume a larger line size.

Locate in Nomograph 3 the pipe diameter and the air volume found in Nomograph 1. A line between these two points yields the

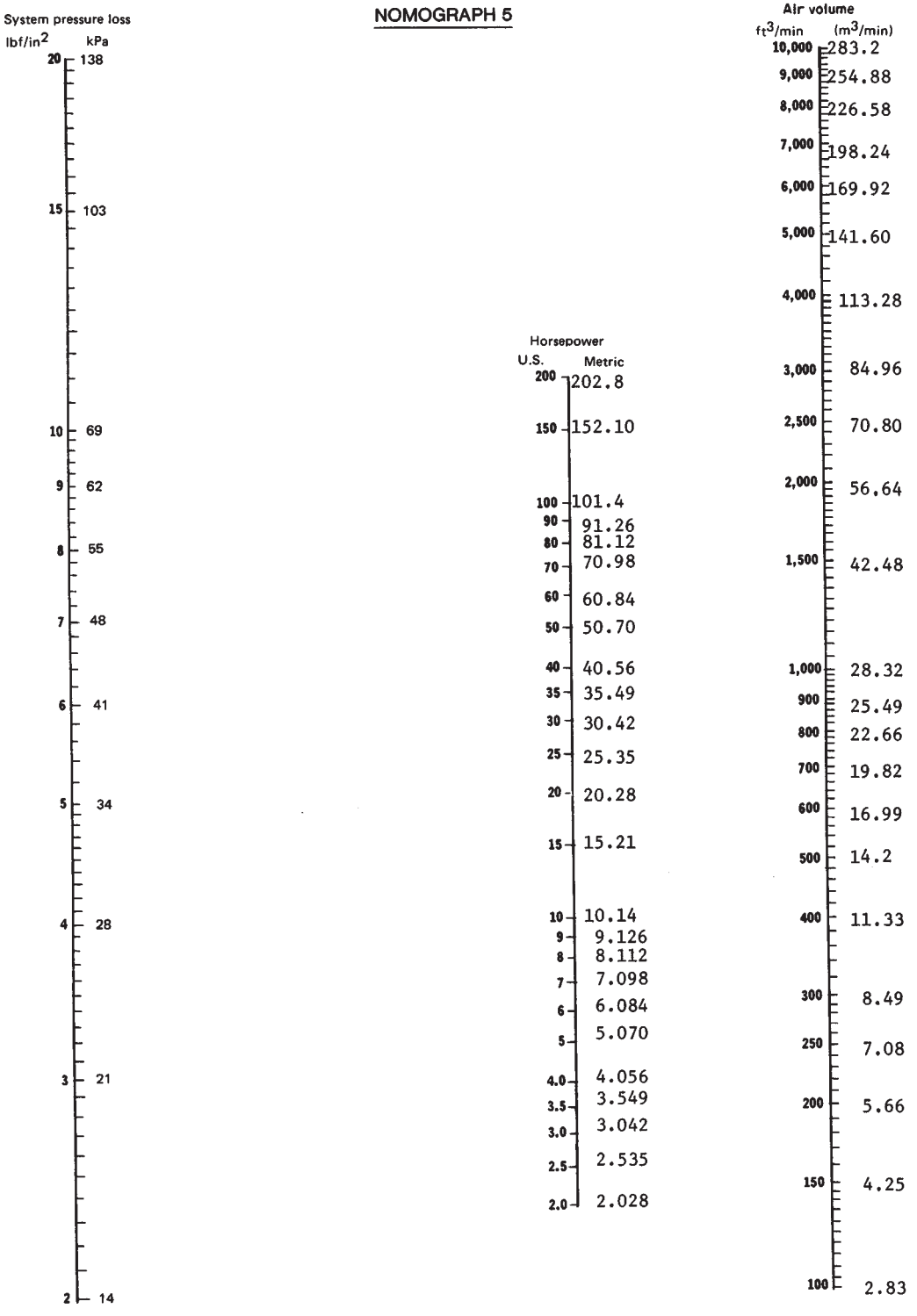


FIG. 21-13 (*Continued*)

TABLE 21-13 Air Velocities Needed to Convey Solids of Various Bulk Densities*

Bulk density		Air velocity		Bulk density		Air velocity	
lb/ft³	kg/m³	ft/min	m/min	lb/ft³	kg/m³	ft/min	m/min
10	160	2900	884	70	1120	7700	2347
15	240	3590	1094	75	1200	8000	2438
20	320	4120	1256	80	1280	8250	2515
25	400	4600	1402	85	1360	8500	2591
30	480	5050	1539	90	1440	8700	2652
35	560	5500	1676	95	1520	9000	2743
40	640	5840	1780	100	1600	9200	2804
45	720	6175	1882	105	1680	9450	2880
50	800	6500	1981	110	1760	9700	2957
55	880	6800	2072	115	1840	9900	3118
60	960	7150	2179	120	1920	10500	3200
65	1040	7450	2270				

*Courtesy of Flotronics Division, Allied industries.

design factor, or P 100 (30.5), the pressure drop per 100 ft (30.5 m), at the intersection of the center scale.

Locating now in their respective scales on Nomograph 4 the design factor (from Nomograph 3) and the calculated equivalent length, draw an extended straight line to intersect the pivot line in the center. Now connect this point in the pivot line with the solids-ratio scale (from Nomograph 2), and read the system pressure loss.

If the value of this loss exceeds 10 lb/in² (70 kPa), assume a larger pipe diameter and repeat all these steps, beginning with Nomograph 1. After a pressure drop of 10 lb/in² (70 kPa) or less is found, turn to Nomograph 5 and locate this pressure loss, as well as the corresponding air volume (from Nomograph 2), and draw a straight line between the two points. The intersection of the horsepower scale will provide the value of the power required. From this, the system cost can now be approximated by consulting Table 21-12.

STORAGE AND WEIGHING OF SOLIDS IN BULK

STORAGE PILES

Discharge Arrangements Open-yard storage is probably best handled by belt conveyor when tonnages are large. Figure 21-14 shows some of the many discharge arrangements possible for single, multiple, or moving-tripper discharge from belt conveyors. Also shown is a tilting-plow arrangement for discharging flat belts. Most of these discharge methods are equally applicable for indoor storage. Large traveling stackers may also be used for outdoor storage. They may move along the length of a belt, forming a pile on one or both sides of the belt, or pivot about a fixed axis to form a circular pile.

Reclaiming Underground-tunnel belts fed by special gates (Fig. 21-15) are often used for reclaiming, as is mobile shovel equipment. Cable-drag scrapers are also used for large outside storage areas and sometimes on inside storage when large, flat areas are used. A drag-scraper system may follow a single fixed cable line, or back posts may be provided to allow relocation of the cable line to cover almost any storage-space shape.

One development for handling large tonnages of bulk materials from storage is the **bucket-wheel reclaimer,** which consists of a series of buckets placed about the periphery of a large wheel that is carried by a fixed propulsion unit. The buckets empty onto a removal conveyor, usually of the belt type, which takes the product to further processing or handling. Bucket-wheel reclaimers capable of handling as little as 150 tons/h to as much as 20,000 tons/h (see Fig. 21-16) have been built.

Mobile equipment is often preferred to fixed types. Front-end loaders, scrapers, and bulldozers are used with increasing frequency, especially on projects of short duration or when capital investment must be limited. Front-end loaders are especially advantageous because of their ability to carry material as well as to plow or bulldoze it.

Angle of repose is the angle at which a material will rest on a pile. It is useful for determining the capacity of a bin or a pile. The angle of the cone that develops at the top of the pile when a bin is being filled will be somewhat flatter than the angle of repose because of the effect of impact.

STORAGE BINS, SILOS, AND HOPPERS

Probably no section of the materials-handling and -storage art advanced as far in a decade (the 1960s) as did that of bin storage of bulk materials. Prior to this time, **storage-bin design** was a hit-or-miss empirical affair, in which success was assured only if the product was free-flowing. This was changed radically as a result of research led by Andrew W. Jenike. This work, which resulted in identifying the criteria that affect material flow in storage vessels, was first reported in Jenike's paper "Gravity Flow of Bulk Solids" (Bull. 108, University of Utah Engineering Experiment Station, October 1961). This paper set forth the equations defining bulk flow and the coefficients affecting flow.

Continuing experimentation verified these criteria, and in Bulletin 123 (November 1964) the subject was further defined by providing flow factors for a number of bin-hopper designs as well as specifications for determining experimentally the characteristics of bulk material affecting flow and storage. Along with the theory, Jenike produced a method of applying it, which includes equations and the physical measurement of material characteristics.

In what follows, a storage vessel is considered as consisting of a bin and a hopper. A bin is the upper section of the vessel and has vertical sides. The hopper, which has at least one sloping side, is the section between the bin and the outlet of the vessel.

Material-Flow Characteristics Two important definitions of the flow characteristics of a storage vessel are **mass flow,** which means that all the material in the vessel moves whenever any is withdrawn (Fig. 21-17), and **funnel flow,** which occurs when only a portion of the material flows (usually in a channel or rathole in the center of the system) when any material is withdrawn (Fig. 21-18). Some typical mass-flow designs are shown in Fig. 21-19.

Mass-flow bins feature the most sought-after characteristics of a storage vessel: unassisted flow whenever the bottom gate is opened. A funnel-flow bin may or may not flow but probably can be made to flow by some means.

Until Jenike developed the rationale for storage-vessel design, a common criterion was to measure the angle of repose, use this value as the hopper angle, and then fit the bin to whatever space was available. Too often, bins were designed from an architectural or structural-engineering viewpoint rather than from the role they were to play in a process. Economy of space is certainly one valid criterion in bin design, but others must be considered equally as well. Table 21-14 compares the principal characteristics of mass-flow and funnel-flow bins.

Although a mass-flow bin is obviously preferable to a funnel-flow vessel, the additional investment generally required must be justified. Often, this can be done by the reduced operating costs. But when installation space is limited, a compromise must be made, such as providing a special hopper design and sometimes even a feeder. Certainly, with mass-flow bins the feeder is not required for flow, but it might still be used for other reasons, such as conveying the material to the next process step.

Design Criteria Jenike's criteria permit an **engineering-economic analysis of storage** with about the same confidence level

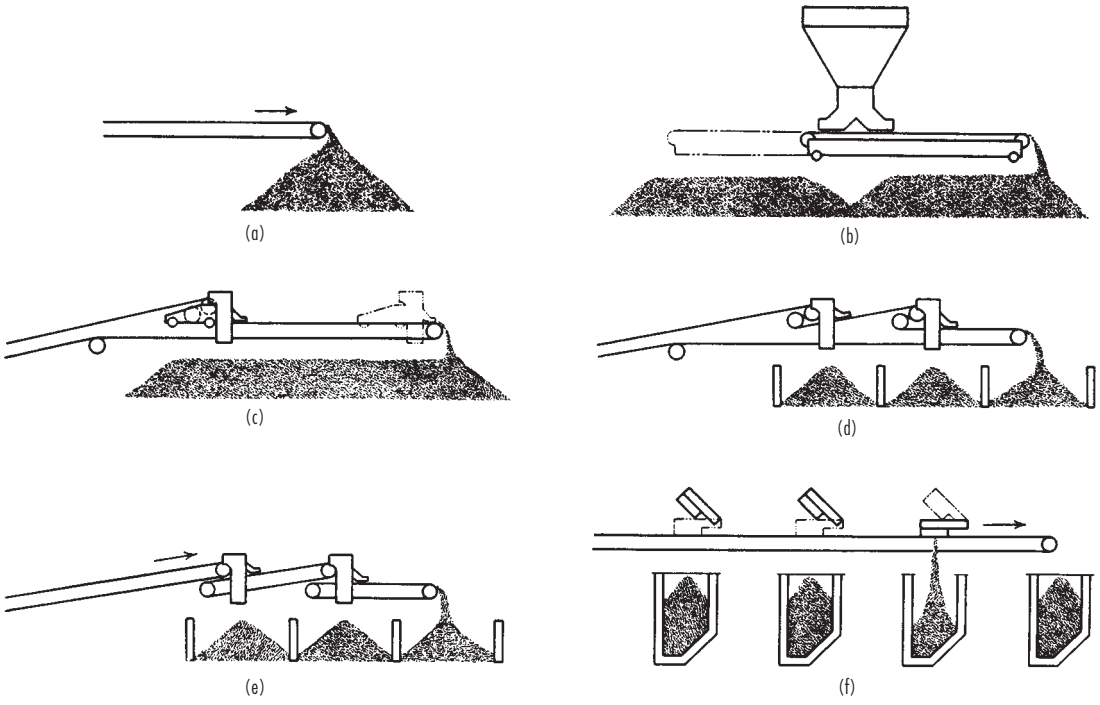


FIG. 21-14 Belt-conveyor discharge arrangements. (*a*) Discharge over an end pulley forms a conical pile at the end of the belt. (*b*) Discharge over either end pulley to distribute lengthwise by a reversible-shuttle conveyor. (*c*) Discharge through a traveling tripper, with or without a cross conveyor, to distribute material to one or both sides of the conveyor for the entire distance of tripper travel. Trippers can be propelled by a conveyor belt or by a separate motor. Motor-propelled trippers can also be automatically reversing to distribute material evenly or can be manually controlled to discharge at any desired point. (*d*) Discharge through fixed trippers, with or without a cross conveyor to one or both sides of the belt, to fixed bin openings or pile locations. This can also be done with multiple conveyors as shown in (*e*) or by stopping traveling trippers in the desired position. (*e*) Discharge from multiple conveyors through fixed discharge chutes, with or without a cross conveyor to one or both sides of the belt, to fixed bin openings or pile locations. (*f*) Discharge by hinged plows to one or more fixed locations along one or both sides of the conveyor. Plows may be adjusted to divide the discharge in several places simultaneously in the proportion desired. (*FMC Corporation, Material Handling Systems Division.*)

as in the rest of the process plant. His quantitative methods may be used to determine (1) whether the vessel will function with mass or funnel flow and (2) the outlet dimensions of the hopper so that product will flow. His methods also provide criteria for making engineering trade-offs between mass flow and funnel flow when product characteristics, space limitations, etc., dictate against design for mass flow.

The **relation between mass and funnel flows** for conical bins is shown in Fig. 21-20. The angle of kinematic friction ϕ', which is a measure of the friction coefficient between the solid and the material of construction used for the conical-shaped hopper, is measured with the "flow-factor tester." The degree of finish of the metal surface can have a large effect in determining whether the vessel will function in mass or funnel flow. Finer degrees of finish are being used more frequently, mostly because intuition has recommended this course. The kinematic angle of friction is also related to the degree of compression that the product undergoes in storage.

Once a decision for mass or funnel flow has been made or a compromise made by including an expanded-flow bin, the hopper outlet and the type of feeder must be considered. Jenike's teaching on the flow through the bin opening is that materials that can be compacted (as opposed to being free-flowing) will be compacted because of storage-vessel shape and the packing characteristics of the product. When this happens, the material forms an arch that is capable of withstanding considerable stress.

Since the arch transfers the load to the hopper walls and in doing so applies so much pressure to them, the kinematic coefficient of friction

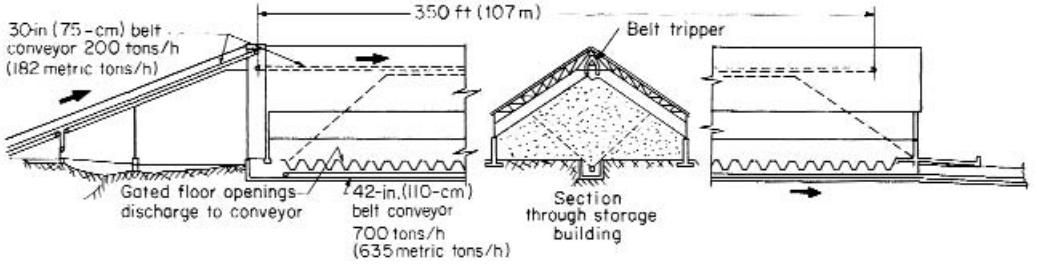


FIG. 21-15 Belt-conveyor storage and reclaiming in a flat-floor building. (*Stephens-Adamson Division, Allis-Chalmers Corporation.*)

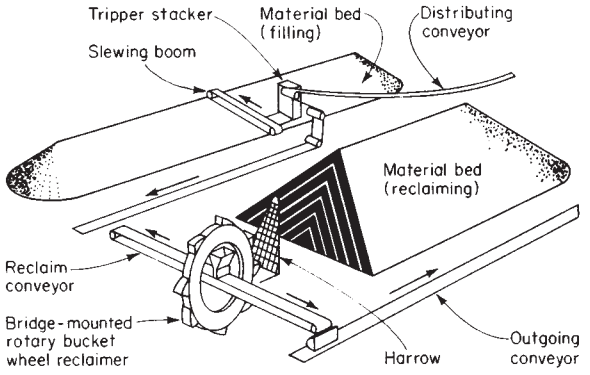


FIG. 21-16 Bucket-wheel reclaimer. Digging buckets mounted on wheel discharge on a belt conveyor for material transfer. (*Courtesy of* Mechanical Engineering.)

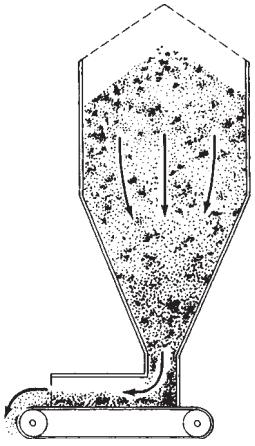


FIG. 21-17 Mass-flow bin. The material does not channel on discharge. (*Courtesy of* Chemical Engineering.)

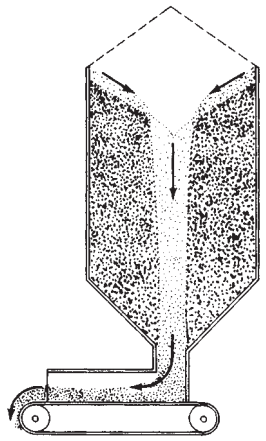


FIG. 21-18 Funnel-flow bin. The material segregates and develops ratholes. (*Courtesy of* Chemical Engineering.)

ϕ' becomes great. The net result is that the "dome" or "bridge" that forms prevents any flow from the vessel. Force must then be applied to the arch so that it will collapse and flow will begin, even if erratically.

According to Jenike, when the strength of the arch f is exceeded by the internal stress s generated by a force applied above the dome, flow takes place. Summarizing:

When $f < s$, flow occurs.

When $f > s$, there is no flow.

When $f = s$, the critical point is reached.

To make a **flow analysis** when $f < s$, an element of material is observed as it moves through a storage vessel (Fig. 21-21). The pressure p on the element increases from zero at the entrance to a maximum value at the transition from the bin to the hopper. The pressure then decreases to zero linearly at the vertex of the hopper cone. The resultant strength f follows a similar pattern, though usually it has some value greater than zero. The stresses induced in the material in the hopper bottom by the weight of material above it are constant but decrease linearly to zero at the cone vertex. The f and s curves intersect at a point corresponding to the critical dimensions of the **bin opening** B.

Reducing this analysis to a technique for determining B, Jenike's method provides a practical way to measure and interpret the strength

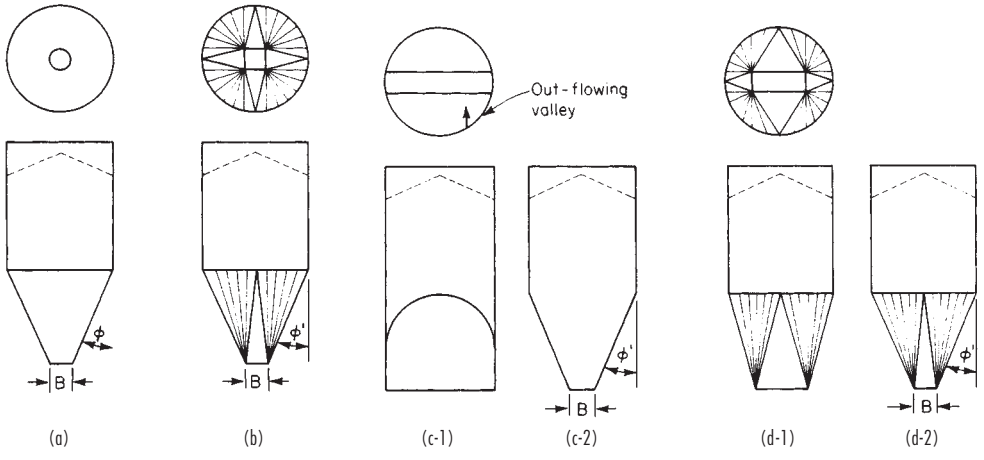


FIG. 21-19 Types of mass-flow bins. Type c is simple but has a valley. Although more difficult to make, type d has no valleys and is usually recommended. (*Courtesy of* Mechanical Engineering.)

TABLE 21-14 Principal Characteristics of Mass-Flow and Funnel-Flow Bins

Mass-flow bins	Funnel-flow bins
1. Particles segregate, but remit on discharge	1. Particles segregate and remain segregated
2. Powders deaerate and do not flood when the system discharges	2. First portion in is last one out
3. Flow is uniform	3. Product can remain in dead zones until complete cleanout of the system
4. Density of flow is constant	4. Product tends to bridge or arch, and then to rat-hole when discharging
5. Level indicators work reliably	5. Flow is erratic
6. Product does not remain in dead zones, where degradation can occur	6. Density can vary
7. Bin can be designed to yield non-segregating storage, or to function as a blender	7. Level indicators must be placed in critical positions so they will work properly
	8. Bins perform satisfactorily with free-flowing, large-particle solids

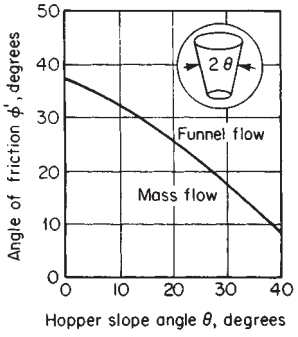


FIG. 21-20 Relation between mass and funnel flows for conical bins. (*Courtesy of* Chemical Engineering.)

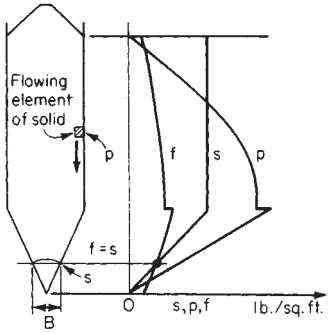


FIG. 21-21 Flow analysis is made by observing an element of material as it moves through the bin. (*Courtesy of* Chemical Engineering.)

of a bulk solid as a function of consolidating pressure. To develop this relation, Jenike developed a **shear tester** that gives a flow function *FF,* which is a curve through a locus of points resulting from values of *f* and *p* obtained by the shear tester. This *FF* curve is plotted against a flow factor *ff* for the particular hopper being designed, as shown in Fig. 21-22.

The method makes use of the principle that a constant ratio of induced stress *s* in the stored contents to the consolidating pressure *p* exists. Thus, for any hopper design for which the *ff* curve is available, the shear-tester results can be plotted, and the point where $f = s$ is located. Since the distance at which this occurs above the hopper vertex is also known, these values become the hopper dimensions at that point.

A useful approximation of *B* for a conical hopper is $B = 22f/\alpha$, where α is the bulk density of the stored product. The apparatus for determining the properties of solids has been developed and is offered for sale by the consulting firm of Jenike and Johansen, Winchester, Massachusetts, which also performs these tests on a contract basis. The flow-factor *FF* tester, a constant-rate-of-strain, direct-shear-type machine, gives the locus of points for the *FF* curve as well as ϕ', the

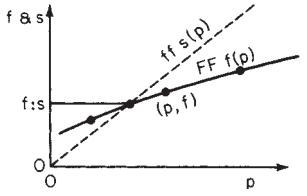


FIG. 21-22 Flow takes place only where *FF* lies below *ff.* (*Courtesy of* Chemical Engineering.)

kinematic coefficient of friction. A consolidating bench is used to prepare samples having different degrees of compaction for the flow-factor tester. This can be supplemented with the same bench enclosed in a controlled-temperature cabinet.

It is possible for some materials to produce an *FF* plot having no intersection with the *ff* curve. This indicates that a different hopper-bin design is needed or that the material cannot be made to flow. Figure 21-23 shows *FF* curves for several materials.

Jenike's method allows the chemical engineer to design bulk-storage vessels and to weigh cost versus performance with a high level of confidence that if the conditions in the real storage system are the same as those prevailing during the tests, the product will flow. It is up to the engineer, however, to establish the bounds of conditions that the product will encounter and to make appropriate tests. A product may not flow if its characteristics change, if radical temperature changes are encountered at the plant, or if moisture is left from an underdesigned dryer.

A further use of the Jenike method is its extension to the critical **structural design** of storage vessels. Because pressures can be calculated, it is possible to design for actual conditions rather than estimates. Also, flow-corrective devices may be designed by using his theory.

Specifying Bulk Materials for Best Flow Many flow problems can be eliminated at the source by rigid, accurate, and sensible specification of the physical characteristics of the material.

Particle size is one of the most common and controllable factors which affect the flowability of a given material. In general, it may be assumed that the larger the particle size and the freer the material is from fines, the more easily the material will flow. Specifications can dictate the desired particle size and uniformity of particle size for purchased raw materials. Stage grinding in the plant can reduce waste and improve flowability by producing a ground material with a mini-

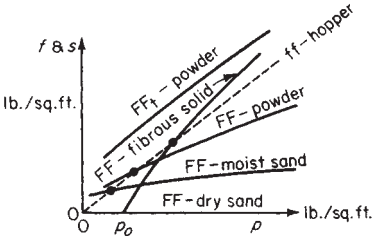


FIG. 21-23 *FF* curves for various materials. Multiply pounds-force per square foot by 0.0479 to get kilopascals. (*Courtesy of* Chemical Engineering.)

mum of fines, but this involves extra operations which may not be economically defensible.

Handling ease is often enhanced by **pelleting** the raw materials. The large particle size, uniformity of particle size, and hard, smooth surface of pellets all contribute to good flow.

Moisture content is another common and controllable flow factor. Most materials can safely absorb moisture up to a certain point; further addition of moisture can cause significant flow problems. Specifications can control the amount of moisture content present in purchased raw materials. Moisture content can be lowered in the plant by including a drying operation in the process line. The costs incurred in drying may be offset by more efficient flow, lower shipping cost, and control of deterioration losses.

Moisture control can also be effected by replacing the air in the material container or bin with a dry, stable gas—nitrogen, for example. This technique is also used to protect the material from certain types of deterioration, such as vitamin loss from food materials.

High temperatures can cause serious flow problems in some materials which contain glutens, sugars, or other soluble or low-melting-point components. These materials become sticky at high temperatures, and it may be necessary to install cooling equipment. As with drying equipment, a study should be made to determine if the additional cost of cooling can be offset by the savings effected by improved flow. Other possible advantages, such as the keeping qualities of the product at lower temperatures, should of course be considered.

Age appears to improve the flowability of certain materials. This is probably the result of particle-surface oxidation, more even moisture distribution, and the rounding of particle corners caused by handling.

Oil content does not materially decrease flowability. For example, the addition of oils and fats to animal-feed ingredients improves the quality of pellets made from these materials, making the pellet surfaces harder and enabling the pellets to resist attrition.

Gates (Fig. 21-24) are used to control flow from bins, hoppers, and processing equipment to feeders or directly to conveyors. They are available in a wide range of styles, from the simple hand slide gate (which can frequently be very difficult to operate by hand) to the precision rack-and-pinion design, which is usually tightly sealed against dust and dribble. The rack-and-pinion gate operates manually with a minimum of effort and is easily adapted to electric, pneumatic, or hydraulic operation. The lever-operated quadrant gate is most often used when a quick-opening gate is desired. It is not designed to control the flow of material but rather to allow the free discharge of lumpy materials. There are hundreds of gate styles to select from, and when properly applied they can often eliminate the need for a more expensive feeder.

Solids-level controls are important for determining the level of materials in bins and hoppers and can also protect conveyors from damage due to jamming if placed in transfer and discharge chutes. They may simply activate an audio or visual warning signal, or they may be electrically tied into the conveying system to start or stop conveyors automatically. Many designs are available, based on principles such as ultrasonics, lasers, radar, and switches operated by diaphragms or paddles. The two designs shown in Fig. 21-25 depend on limit switches, with activation from a pendant cone on one and from a stainless-steel diaphragm on the other. In either case, the presence of material resting against the cone or diaphragm opens or closes the switch, activating a warning signal in the latter case and turning off power to the conveyor in the former.

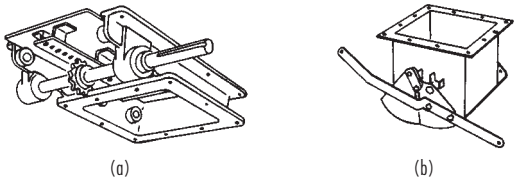


FIG. 21-24 (*a*) Rack-and-pinion gate. (*b*) Double-quadrant gate.

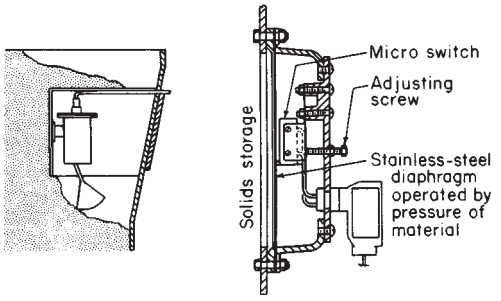


FIG. 21-25 Bin-level-control units.

FLOW-ASSISTING DEVICES AND FEEDERS

Often there are situations in which mass-flow bins cannot be installed for reasons such as space limitations and capacity requirements. Also, sometimes the product to be stored has an *FF* flow function that lies below the flow factor *ff*, bridging takes place, and unassisted mass flow is not possible. To handle these situations, a number of **flow assisters** are available, the most desirable of which use a feeder and a short mass-flow hopper to enlarge the flow channel of a funnel-flow bin. The choice of feeder or flow assister should always be made as part of the storage-vessel analysis. The resulting systems are then usually as effective as the mass-flow types.

Vibrating hoppers are one of the most important and versatile flow assisters. They are used to enlarge the storage-bin opening and to cause flow by breaking up material bridges. Figure 21-26 shows this type of feeder. Two basic types of vibrating hoppers are common: the gyrating kind, in which vibration is applied perpendicularly to the flow channel, and the whirlpool type, which by providing a combined twist and lift to the material, causes bridging to break. One version of this type of flow assister is a bin that vibrates or oscillates in its entirety. Such bins are usually limited to a capacity of about 2.8 m^3 (100 ft^3).

Screw feeders are also used to assist in bin unloading and in producing uniform feed. Of importance here is the need for a variable-pitch screw to produce a uniform draw of material across the entire hopper opening (Fig. 21-27). For uniform flow to occur, the screw-feeder opening-to-diameter ratio should not exceed 6.

Belt or apron feeders can also be used to give uniform feed from a bin, but care must be taken that dead spots are not produced in the

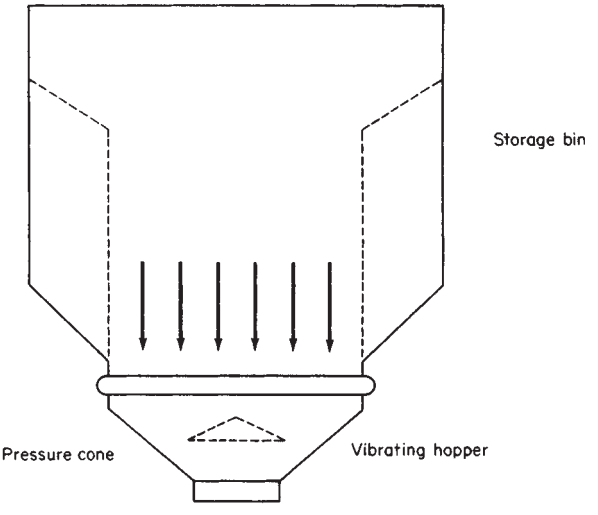


FIG. 21-26 Vibrating hopper. It enlarges the storage-bin opening and breaks up material bridging. (*Courtesy of* Mechanical Engineering.)

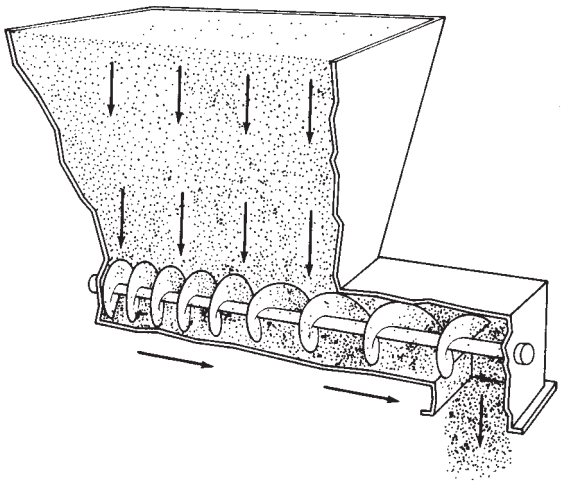


FIG. 21-27 Screw feeder. It needs a variable-pitch screw to produce a uniform draw of material. (*Courtesy of* Chemical Engineering.)

flow channel above the feeder belt (Fig. 21-28). The capacities of these feeders can be increased by tapering the outlet in the horizontal and vertical planes. To ensure the flow of non-free-flowing solids along the front bin wall, a sloping striker plate at the front of the hopper is necessary. Taper may be in one direction only. An apron feeder for large rock, for instance, would have bin skirts tight against the pan to prevent the rock from wedging between the hopper and feeder, and the taper would be in the horizontal plane only. For long slots, however, increasing slot width to provide taper becomes impractical.

Belts have been used successfully under slot openings as long as 30 m (100 ft), with a constant slot width of 205 mm (8 in). Provisions should be made for field adjustment of the space between the skirt and the belt to provide uniform flow along the entire length. Since the minimum distance between the skirt and the belt should allow the largest particle to pass under, very long belt feeders are limited to the finer solids.

The same principles apply to **table feeders.** The skirt is raised above the table in a spiral pattern to provide increased capacity in the direction of rotation (Fig. 21-29). The plow, located outside the bin, plows only the material that flows from under the skirt.

Vibratory feeders also provide uniform flow along a slot opening of limited length (Fig. 21-30). Here also, the distance between the feeder pan and the hopper is increased in the feed direction. Slot length is limited by the motion of the feeder. Because in long slots the upward component of motion is not relieved by the front opening, solids tend to pack. This can cause flow problems with sticky solids as well as a large demand of power for free-flowing materials. To circumvent these difficulties, vibratory feeders and reciprocating-plate feeders are designed to feed across the slot. Although this kind of feeder may require several drives to accommodate extreme width, the drives are small because of the feeder's short length.

Star feeders with a collecting-screw conveyor (Fig. 21-31) provide highly uniform withdrawal along a slot opening. A vertical section of at least one outlet width should be added above the feeder to ensure uniform withdrawal across the opening.

Other methods of aiding bin unloading are rotating-arm units and air fluidizing pads.

WEIGHING OF BULK SOLIDS

Automatic weighing has largely replaced manual weighing in the chemical-process industries because of the advent of larger-capacity processes and the need to economize on labor. Also, the dependability of weighing equipment has increased markedly, and investment cost has decreased. Both batch and continuous weighing are used.

Batch Weighing In batch weighing, a given unit of weight is measured, and then the desired total weight is obtained through multiples of the given unit. Batching scales find use when small weighings are carried out either singly or a few in sequence.

Most batch scales involve a vessel mounted on a weigh beam, which is counterbalanced by a set of weights approximately equal to the desired weighing. A feed source mounted over the weigh vessel is activated or stopped by a signal generated by motion of the scale beam. Straight mechanical scale-control systems have largely been replaced by those having air or hydraulic-cylinder control of the feed source and weigh-vessel discharge. These are activated by electrical controls.

The **principle of operation** of batch-type scales is based on the concept that a flowing stream of material has constant density. If this is true, then if at some point in advance of the desired batch weight the stream is cut off, the amount of material flowing will remain con-

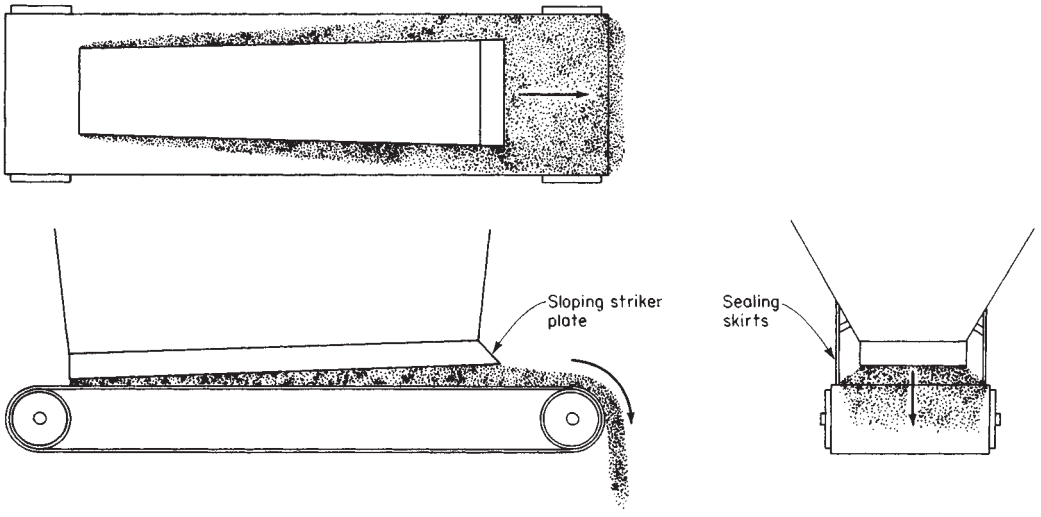


FIG. 21-28 Sloping striker plate in the belt of an apron feeder ensures the flow of non-free-flowing solids. (*Courtesy of* Chemical Engineering.)

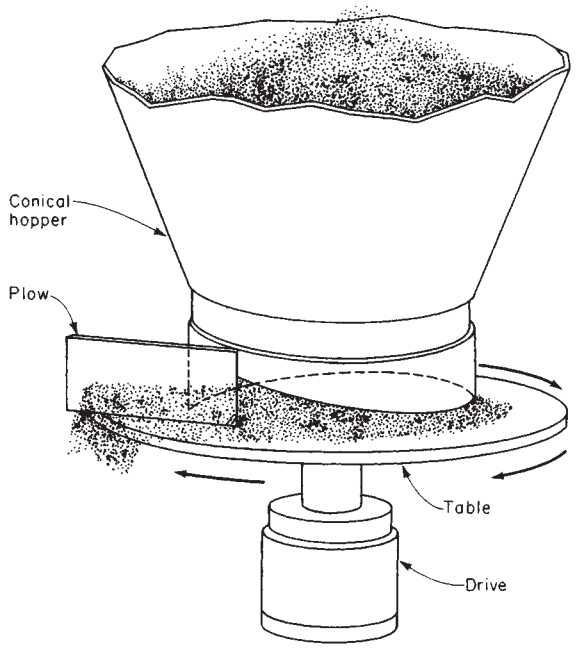


FIG. 21-29 Table feeder. The skirt is raised in a spiral pattern for increased capacity in the direction of rotation. (*Courtesy of* Chemical Engineering.)

stant between the time when the weight is sensed and the time when the flow is stopped. The total weight in the weigh vessel is the sum of the charge due to flow and the amount that flows during the cutoff period. For this reason, feed conditions to the scale are important. **Uniform flow** is essential for accurate batch weighings.

If the material is free-flowing, a mass-flow hopper (Fig. 21-32) can be used. If it is not free-flowing, an appropriate feeder such as a screw,

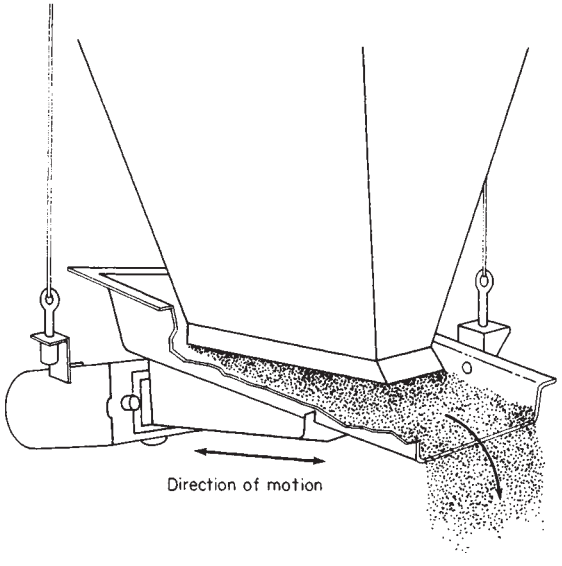


FIG. 21-30 Vibratory feeder. The distance between the feeder pan and the hopper is increased in the direction of feed. (*Courtesy of* Chemical Engineering.)

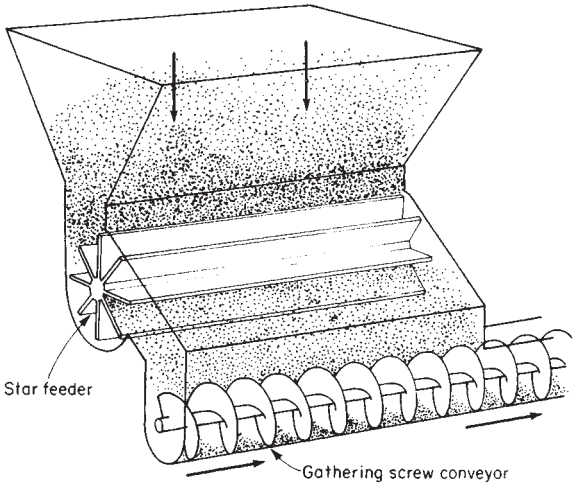


FIG. 21-31 Star feeder. The collecting screw ensures uniform withdrawal. (*Courtesy of* Chemical Engineering.)

belt, or vibratory feeder should be used. These feeders are described in the subsection "Flow-Assisting Devices and Feeders."

Of special interest in scale-control systems is the type in which the motion of the scale beam is sensed by a differential transformer or a group of load cells. The output of such devices is proportional to the displacement of the scale beam, which in turn is proportional to the amount of material in the weigh bucket. Many designs use load-sensing devices such as strain gauges or transducers. These eliminate the need for a scale-beam mechanism. The weigh vessel is mounted directly on the load-sensing devices. This provides many benefits in

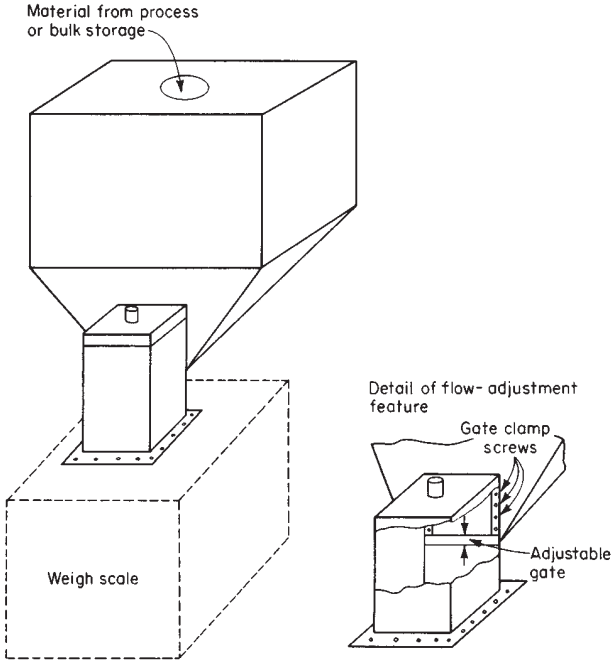


FIG. 21-32 Mass-flow hopper for free-flowing products, used with simultaneous fill-and-weigh and preweigh scales.

addition to accurate weights. One of the most notable is the ability to use the output to indicate actual weight in the weigh vessels or, through a different calibration, to read variations from the desired weight.

Use of microprocessors allows this signal to be employed in a variety of useful ways: controlling weight, adjusting the scale to accommodate the slight changes in bulk density inherent in flowing bulk materials, and activating recording devices, printing heads, and label printers. These features were not possible with straight mechanical scales. Because the microprocessor can perform arithmetic operations and be programmed by using algebraic logic, many products previously considered difficult or impossible to weigh accurately can now be weighed with accuracies equal to those for free-flowing materials. This permits weighing to be done by **addition** or by **subtraction.** With the **additive-**type scale, material is **added** to the weigh vessel, which is being sensed by the scale-control system. With a **loss-of-weight scale,** material flows out of a vessel which is being continuously weighed.

When extreme accuracy of weighings is required, the feed to the weigh vessel is divided into two successive portions: a large **bulk charge,** followed by a final short **dribble feed,** which should have a flow rate of about 0.01 percent of the bulk rate.

A typical application of batch scales is the weighing of charges for packaging machines. Another is the weighing of given amounts of raw material and then dropping these into the next process unit, such as a mixer or an autoclave. Batch weigh scales are capable of a weighing accuracy of within ±0.1 percent when they are equipped with bulk and dribble controls. When also equipped with high-sensitivity weight-sensing devices and microprocessor control, with the latter continuously plotting actual versus desired weight, batch weigh scales are capable of ±0.001 percent accuracy within 3 sigma limits.

Additive Weigh Scale The sequence of operations involved in weighing a charge of material (Fig. 21-33) is as follows. A free-flowing product is available in the scale feed hopper (1). On depressing the manual start switch (19), the bulk gate (5) and the dribble gate (6) open. The product flows into the scale weigh bucket (2). Weight is sensed by strain gauges (13), (14), whose analog output is converted to a digital output by a circuit in the microprocessor (18), which reads the weight X times each second, depending on the sensivity needed. When a preset bulk weight (approximately 98 percent of the desired weight) is reached in the scale bucket (2), the microprocessor closes the bulk gate (5) and opens the dribble gate (6). Dribble feed commences, and when the desired weight is reached, the microprocessor causes the dribble gate to close, completing the weight measurement. The scale bucket gate automatically opens, discharging the product weighed to the next process stage. The microprocessor then displays the actual weight of the charge (20) and records, lists, prints (21), and signals any discrepancy in weight if this is outside the tolerance desired. It also can print a label for the batch if desired.

Loss-of-Weight Scale The sequence of operations in this scale (Fig. 21-34) is as follows: Depressing the initializing switch (1) causes the feeder (2) to fill the weigh hopper (3) until the level-control switch (5) opens, stopping the flow, closing the interlocking switch (5), and measuring and recording the initial weight W_0 in the weigh hopper (3). Depressing the start button (6) causes the feeder (4) and the bag packer to start simultaneously. The product is conveyed by the feeder (4) into the packer (7) and by the bag packer into the bag (not shown). The microprocessor (8) reads the analog-to-digital-converter signal (8), which is connected to the strain-gauge load cell (9), and subtracts weight W_i in the hopper (3) at time t_i from the initial weight W_0. The weight difference W_j is summed and recorded. When $W_j = W_s$, the desired weight, the microprocessor stops the feeder (4) and, X seconds later, the bag packer (7). The microprocessor then displays the value of weight W_f (10) and records, lists, and prints (11) any discrepancy between the desired weight and W_f, the weight actually obtained. The packaging system shown is designed for handling products which have very poor or erratic flow characteristics. In addition to its use with packaging equipment, the **loss-of-weight scale** can be employed for a wide variety of process applications.

Continuous Weighing This procedure involves a device that is sensitive both to the total amount of material flowing and to changes in the flow. The material is continuously brought over the weight-sensing elements of the continuous-weigh scale, which is capable of keeping track of the flow and its changes and eventually accounts for these when totaling them. Continuous-weighing scales use a section of a belt conveyor, over which the material to be weighed passes.

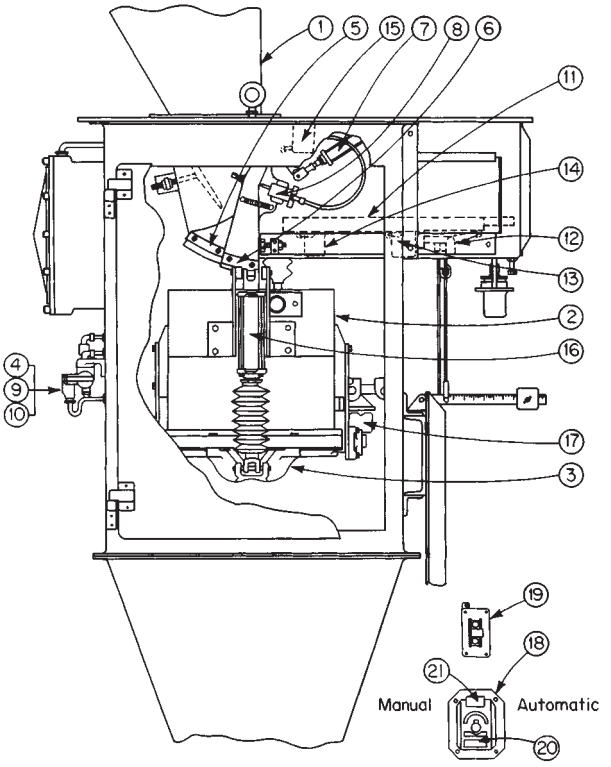


FIG. 21-33 Typical batch-type additive automatic scale. Components: (1) Bin. (2) Scale bucket. (3) Bucket gate. (4) Solenoid valve. (5) Bulk gate. (6) Dribble gate. (7) and (8) Air cylinders powered by solenoid-operated valves. (9) and (10) Solenoid-operated valves. (11) Scale beam. (12) Booster device. (13) and (14) Load cells. (15) Microswitches. (16) Air cylinder. (17) Proximity switch. (18) Microprocessor. (19) Manual start switch. (20) Weight display of the most recent weighing. (21) Average weight display for all weighments of the current product batch.

The belt is mounted on a weight-sensitive platform, typically equipped with load cells, which can detect minute changes in the weight of material passing over the belt. The load-cell output (which is usually a change in resistance proportional to weight) is integrated over short intervals and the condition of flow given. This may be a rate of flow or, at the end of a weight measurement, the total weight. Figure 21-35 shows a continuous weigher, sometimes referred to as a proportioner. Continuous-weighing scales are used mostly to feed materials to continuous processes at uniform, measured rates. They are capable of weighing within ±1 percent error or even within 0.1 percent error under certain conditions.

TABLE 21-15 Weight Sensing Devices and Sensitivity

Device	Sensitivity (one part in)
Beam-Microswitch	1,000
Beam-Differential Transformer	10,000
Strain Gauge Type Load Cell	20,000
Magnetic Force Restoration Transducer	500,000
Variable Capacitance Transducer	1,000,000

Data courtesy of Kg Systems, Inc., Bloomfield, NJ.

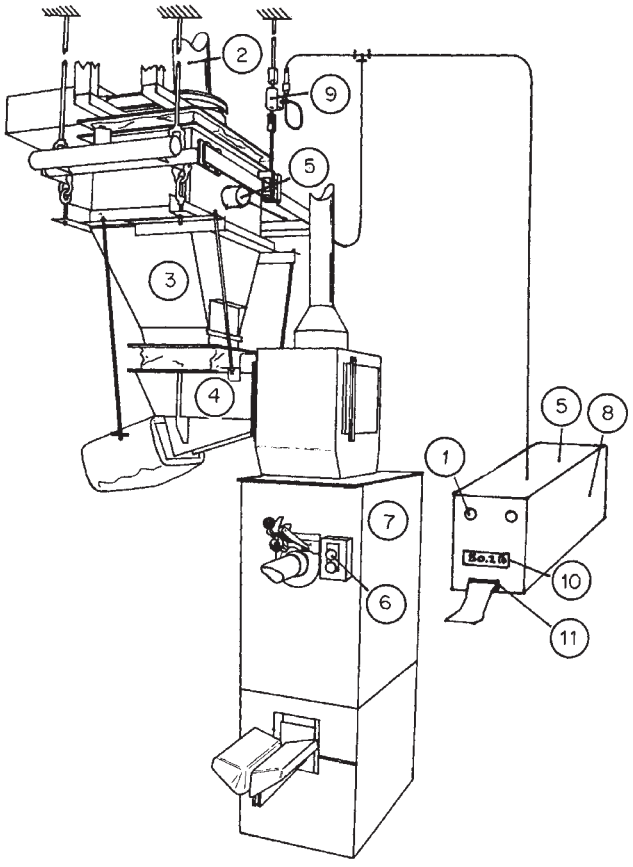


FIG. 21-34 Loss-of-weight-type scale used with a bag-packaging machine for non-free-flowing products. (*Courtesy of H. F. Henderson Industries, Inc., Caldwell, NJ.*)

All scales require continuous monitoring to assure that the desired set weight is maintained and does not drift off because of changes in product bulk-density or flow characteristics. Microprocessors can perform this task automatically.

Weight Sensing These devices have been the subject of intensive research, development, and applications. Increased sensitivity and reliability have been the result of this effort, which has been driven by the increased availability of special purpose computers and the data processing capability of low-cost personal computers. Table 21-15 lists those commonly available and gives their sensitivity. As a result of this, custom-designed weighing equipment has become an important alternative to standardized or "off the shelf" designs. This is especially true when there is a necessity to modify a standard design, which often is more expensive than a custom design.

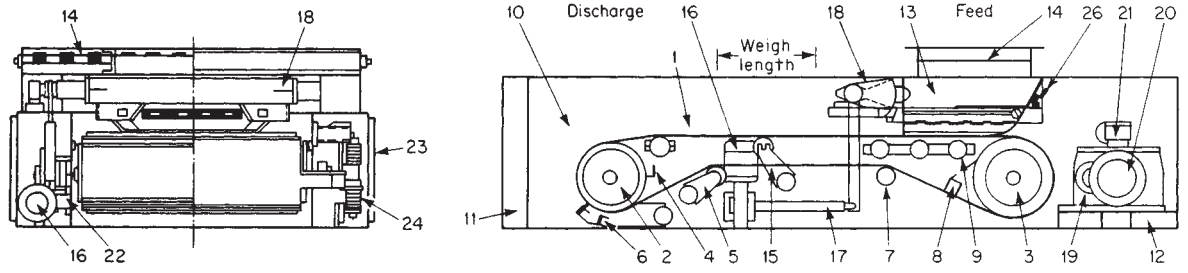


FIG. 21-35 Bulk continuous weigher. (1) Conveyor belt. (2) Head pulley. (3) Tail pulley. (4) Pulley scraper. (5) Spring-loaded take-up assembly. (6) Outer belt scraper (spring-loaded). (7) Belt tracking control. (8) Belt scraper (inner). (9) Pulley scraper. (10) Side channel. (11) Cross channel. (12) Cross channel. (13) Transition chute (optional). (14) Feed-cutoff gates. (15) Weigh idlers. (16) Gate-screw drive motor. (17) Gate screw. (18) Manual gate-adjustment screw. (19) Tachogenerator (optional). (20) Variable-speed drive. (21) Speed adjustment for motor drive (20). (22) Coupling. (23) Side cover. (24) Weight-sensing elements. (25) Hopper storage (optional). (26) Adjustable heel plate (optional). (*Howe Richardson Company.*)

PACKAGING OF SOLID AND LIQUID PRODUCTS AND HANDLING OF PACKAGES

Packaging is often defined by the chemical industry as including all packages or containers which will hold 2 metric tons (4400 lb) of product or less. These containers include bags, cartons, drums and pails, cans, bottles, bulk bags, and metal tanks. Materials of construction can be paper, plastic, metal, glass, wood, or composites of these. A representative list showing the wide variety of containers available for chemical products is given in Table 21-16, which includes typical specifications and representative 1995 costs.

Packaging information has assumed a new importance as the chemical industry in the United States has downsized and the position of the professional packaging engineer has virtually disappeared. Often, the chemical engineer without packaging experience is faced with a project in which the package must be designed and specified and the packaging machinery chosen. Useful sources of information are texts which deal specifically with the subject of packaging. Prominent among these are: *The Wiley Handbook of Packaging Engineering*, published by John Wiley & Sons; *The Handbook of Packaging Engineering* by Joseph Hanlon, published by Technomic Publishing Co., Inc.; and *Fundamentals of Packaging Technology* by Walter Soroka, published by the Institute of Packaging Professionals (IOPP). These and other useful texts are sold by the packaging bookstore of IOPP which has an extensive catalog available. The *IOPP Directory of Packaging Consultants* gives services and skills available in chemical packaging and labeling. Address: Institute of Packaging Professionals, 481 Carlisle Drive, Herndon, VA 22070-4823, 703-318-8970, FAX 703-318-0310.

The Gottscho Packaging Information Center at Rutgers, The State University of New Jersey, College of Engineering, Center for Packaging Science and Engineering, Building 3529, Busch Campus, Piscataway, NJ 08855 is a unique library devoted to packaging and related subjects. A literature search service is available.

Ecology concerns have resulted from an environmentally conscious world. In many countries, laws regulate the type of packaging that can be used and the manner in which it must be disposed of. In Europe, the German packaging law has become a model for the control of packaging and its disposal. It has been copied by many nations. While consumer packaging is the principal aim of this law, industrial packaging is also controlled. Arrangements must be made for the safe and approved disposal of used packaging. The effect of this has caused the chemical industry to reexamine whether disposable packaging should be used in view of the cost of disposal. By way of example, a wood pallet, used to contain one metric ton of product in multiwall paper bags, might have a purchase price in the United States of $12.00. The disposal costs for such a pallet could range between $30 and $65. This gives rise to the use of returnable packaging components which would also include steel drums and pails, plastic drums and pails, pallets, bulk corrugated boxes, corrugated shipping containers, and woven mesh bulk bags. Because this is such a rapidly changing field it is incumbent on those involved with package design, development, and logistics to know the local regulations where the package will be sent. Logistics is an important consideration. If returnable packages are to be used, their return must be planned and the costs for such return developed. An option for package disposal where returnable packages are involved is to sell them for reuse in the country they are destined for. Further complicating the disposal of packages is any residue of the product which they originally contained. For example, it is not uncommon to find a 55 gal (208 liter) steel drum after unloading, containing a "heel" of 1 to 4 liters of product. The collection and disposal of such materials is highly regulated in the United States by the Environmental Protection Agency (EPA) CFR 40 and state and local laws. Similar regulations are in effect in most of the developed nations.

Regulation of packaging during the past decade has changed significantly. There are more governmental units involved, innumerable regulations which must be complied with, and substantial penalties for failure to comply. This applies to packaging regulations especially in the United States but also in the rest of the world. The United Nations (UN) acts as a worldwide regulatory agency. Most industrialized nations have their own governmental units which regulate packaging based on UN regulations.

In the United States, the Department of Transportation (U.S. DOT) regulates the packaging, handling, and transport of all materials which are regarded as hazardous or dangerous. In addition the Environmental Protection Agency (EPA), the Occupational Safety and Health Act (OSHA), the Food and Drug Administration (FDA), the Nuclear Regulatory Commission (NRC), and the U.S. Department of Agriculture (USDA) all exercise a regulatory influence over packaging for materials or products which by law are mandated to them. Those regulatory agencies with whom the practicing chemical engineer involved with packaging must contend are principally the U.S. DOT and to some extent, the EPA and OSHA. In the pharmaceutical and food industries, the FDA is the primary regulator. In the alcoholic beverages industry, the U.S. Department of the Treasury's Bureau of Alcohol, Tobacco, and Firearms (ATF) branch regulates the packaging used for these products. Most notably, however, is the impact of the regulations of the U.S. DOT. During the past two decades the U.S. DOT has changed the approach to packaging regulations from one of strict packaging material specifications to that of requiring specific package performance. Under the former, construction features of a package required for a specific hazardous material was spelled out in minute detail. Under the performance-packaging approach the same size and type container must now be capable of handling performance tests without failure for the particular packing group that is required for the hazardous nature of the product.

The specific regulations of the U.S. DOT are found in the Code of Federal Regulations (CFR) Title 49, Parts 100–199. A key part of CFR 49 is Part 172.101 a portion which is illustrated as Table 21-17.

Where a product is not deemed as hazardous and thus not regulated by any of the above governmental bodies, in the United States, acceptable packaging is defined by industry associations for the different transportation modes which might transport the product. Their interest is in protecting the product from damage and, consequently, claims against the transportation companies for improper handling and for loss or damage to the product. The National Motor Freight Classification (NMFC) of the American Trucking Associations, Inc. and the Uniform Freight Classification of the Association of American Railroads are two such regulatory bodies. Failure to comply with their regulations does not carry the penalties of law, but it does allow the transportation company to disallow payment of claims for loss or damage to freight while in their care. In addition to these, other agencies are involved in the regulation of packaging. Table 21-18 summarizes these.

The CFRs can be obtained from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, telephone 202-783-3238. The National Motor Freight Commission booklet 6000 may be obtained from the American Trucking Associations, Inc., 7200 Mill Road, Alexandria, VA 22314. The Uniform Freight classification, ratings, rules, and regulations for railroad shipment can be obtained from the Uniform Freight Classification Commission, Tariff Publishing Officer, Suite 1160, 222 South Riverside Place, Chicago, IL 60606. UN regulations are contained in the publication *Recommendations on the Transport of Dangerous Goods*, which is available from the UN Publications Section, UN Plaza, New York, NY 10017.

The United States has moved to follow the approach established by the United Nations to performance-based specifications for the packaging and packaging materials used for hazardous materials. The U.S. DOT, through Rule Making Docket HM 181 defined the United States position for performance-oriented packaging. Through many hearings and requests for industry comment, the DOT has now published in CFR 49 the changes necessary to bring U.S. packaging specification for hazardous materials in compliance with the United Nations specifications.

The nature of the change to performance-tested packaging is best illustrated with an example of a shipment of ethyl alcohol in a 55-gallon (208 liter) steel drum. Under the old rules one could look up

TABLE 21-16 Typical 1996 Cost of Containers for Chemical Products

Container size and description	Unit cost,[i] US$	Usable volume ft³	Usable volume m³	Remarks
Metal drums[a,b,c]				
55 gal (208 L), steel, tight head, 18-20-18 gauge,[d] DOT-P.G. II	$50.15	7.35	0.208	
55 gal (208 L), steel, tight head, all 16 gauge, DOT P.G. I	75.00	7.35	0.208	
55 gal (208 L), steel, open head, 18 gauge, Rule 40[e]	55.71	7.35	0.208	
55 gal (208 L), steel, open head, 16-18-18 gauge, DOT-P.G. III	70.15	7.35	0.208	
55 gal (208 L), steel, tight head or open head, 18 or 18-20-18 gauge, used, reconditioned	22.80	7.35	0.208	
55 gal (208 L), Type 304 stainless steel, tight head, 16 gauge, DOT P.G. I	985.00	7.35	0.208	
30 gal (113 L), steel, tight head, 20 gauge, DOT	41.28	4.00	0.113	
30 gal (113 L), steel, open head, 20 gauge, Rule 40[e]	33.23	4.00	0.113	
16 gal (61 L), steel, open head, lug cover, without fittings, 22 gauge	21.71	2.14	0.061	
55 gal (208 L), steel, dip-galvanized, tight head, 18 gauge, DOT	100.00	7.35	0.208	
56.1 gal (204 L), steel, with 40-mil PE insert, external fittings, 18-20-18 gauge, 55-gal usable volume, DOT, open head[e]	89.00	7.20	0.204	
56.1 gal (204 L), but tight head	90.75	7.20	0.204	
55 gal (208 L), of blow-molded high-density PE,	45.15	7.20	0.204	
Cans and pails[b]				
Pail, 5 gal (19 L), steel, tight head, 26 gauge, black steel, PE pour spout, unlined	$10.91	0.67	0.019	
Pail, 5 gal (19 L), 26 gauge, black steel, open head, unlined, lug cover, wire-bail handle.	8.15	0.67	0.019	
Can, 1 gal (3.8 L), friction-wedge lid, handle (paint can)	1.90	0.1335	0.004	
Can, 1 qt (0.95 L), friction-wedge lid (paint can)	0.79	0.034	0.001	
Can, 1 gal (3.8 L), oblong F style, handle, 1¼-in (32-mm) screw cap	2.90	0.1335	0.004	
Can, 1 pt (0.48 L), oblong F style, 1-in (25-mm) screw cap	1.05	0.0167	0.0005	
Square can, 5 gal (20 L), blow-molded PE with 2¾-in cap (often called "5-gal squares", or Jug)	7.43	0.67	0.019	
Can, 1 pt (0.48 L), round-cone-top style, with 1-in (25-mm) cap	1.15	0.0167	0.0005	
Fiber drums[b,f]				
61 gal (231 L), 9 ply, 400-lb (181-kg) load limit, dry products only, Rule 403	$22.50	8.15	0.231	
55 gal (208 L), 9 ply, 400-lb (181-kg) load limit, dry products only, Rule 403	20.67	7.35	0.208	
47 gal (178 L), 9 ply, 400-lb (181-kg) load limit, dry products only Rule 403	19.89	6.28	0.179	
41 gal (155 L), 9 ply, 400-lb (181-kg) load limit, dry products only, Rule 403	18.24	5.48	0.155	
30 gal (113 L), 9 ply, 400-lb (181-kg) load limit, dry products only, Rule 403	16.20	4.00	0.113	
30 gal (113 L), 7 ply, 225-lb (102-kg) load limit, dry products only, Rule 403	14.48	4.00	0.113	
15 gal (56.8 L), 6 ply, 150-lb (68-kg) load limit, dry products only Rule 403	10.75	2.00	0.057	
55 gal (208 L), 9 ply, PE barrier, 400-lb (181-kg) load limit, Rule 403	21.05	7.35	0.208	
55 gal (208 L), 9 ply, PE-aluminum foil liner, 400-lb (181-kg) load limit, Rule 403	31.32	7.35	0.208	
55 gal (208 L), 10 ply, blow-molded, 15-mil PE liquidtight liner, tight head, steel cover with 2-in and ¾-in NPT1 openings, 600-lb (272-kg) load limit,	47.31	7.35	0.208	
30 gal (113 L), 9 ply, same as preceding except 450-lb (204-kg) load limit	36.51	4.00	0.113	
30 gal (113 L), 8 ply, 300-lb (136-kg) load limit, removable fiber cover, no barrier	17.28	4.00	0.113	
15 gal (56.8 L), 6 ply, same as preceding except 150-lb (68-kg) load limit	11.41	2.00	0.057	
1 gal (3.8 L), 5 ply, same as preceding except 150-lb (68-kg) load limit	5.01	0.1335	0.004	
55 gal (208 L), 9 ply, 400-lb (181-kg) load limit, semisquare removable fiber cover, Ro-Con style	20.21	7.35	0.208	
45 gal (170 L)	12.21	6.01	0.170	

Black steel drums lined at extra cost:

Lining	No. coats	Cost/drum, $
Baked resin, pigmented	1	7.00
	2	9.60
Epoxy phenolic composite	2	11.14

Prices shown include ¾-in and 2-in fittings and are for unlined drums; add $1.25 per drum for delivery.

Approximate steel drums per truckload

55-gal size = 360 drums
30-gal size = 592 drums
16-gal size = 1225 drums

U.S. standard gauge equivalents

Gauge	in	mm
16	0.0598	0.0152
18	0.0478	0.0121
20	0.0359	0.0091
22	0.0299	0.0076
24	0.0239	0.0061

Approximate fiber drums per truckload

61-gal size = 300 drums
55-gal size = 318 drums
47-gal size = 424 drums
41-gal size = 552 drums
30-gal size = 592 drums
15-gal size = 1272 drums
1-gal size = 17,365 drums

Fiber drum type	Outside dimensions: Diameter in	Diameter cm	Height in	Height cm
55-gal lever top	21	53.3	40¾	103.5
55-gal lever top	23½	59.7	30¾	78.1
55 gal lever top	22	55.9	34¾	88.2
41-gal lever top	20½	45.1	30¼	76.8
30-gal lever top	19	48.3	26¼	66.7
6.28-ft³ rectangular	17⅝*	44.8	37½	95.3
55-gal liquid	22	55.9	37½	95.3
30-gal liquid	19	48.3	28	71.1
55-gal fiber	20⅜	51.8	40¾	103.5
30-gal fiber	17⅜	44.1	30¾	78.1

*Side dimension, square.

TABLE 21-16 Typical 1996 Cost of Containers for Chemical Products (*Continued*)

Container size and description	Unit cost, US$	Usable volume, ft³	Usable volume, m³
Bags: multiwall paper and polyethylene film[g]			
Pasted valve bag, 20½-× 22-in face, 5½-in top and bottom (520 × 560 × 140 mm) with 1-mil free film, 2/50, 1/60 kraft, PE internal sleeve	$0.51	1.33	0.038
Sewn valve bag, 15 × 5½ × 30¼ in, 5½-in PE internal sleeve (380 × 140 × 770 × 140 mm) with 1-mil free film, 2/50, 1/60 kraft	0.61	1.33	0.038
Pasted valve bag, 18½ × 22¾ in, 3½-in top and bottom (470 × 580 × 90 mm), PE internal sleeve, 3/50 kraft	0.36	0.84	0.024
Sewn open-mouth bag, 20 × 4 × 30¾ in (510 × 100 × 780 mm), 3/50, 1/60 kraft	0.49	2.00	0.057
Sewn valve bag, 19 × 5 × 33½ in, 5½-in tuck-in sleeve (480 × 130 × 850 × 140 mm), 3/50, 1/60 kraft	0.65	2.00	0.057
Pasted valve bag, 24 × 25¼ in, 8-in top and bottom (610 × 640 × 200 mm), tuck-in sleeve, 3/50, 1/60 kraft	0.61	2.00	0.057
Pasted open-mouth baler bags, 22 × 24 in, 6-in bottom (560 × 610 × 150 mm), 1/130 kraft (or 2/70)	0.36	1.33	0.038
Flat tube open-mouth bag, 10-mil PE film, plain, 20½ × 34¼ in (520 × 870 mm)	0.73	1.33	0.038
Square-end valve bag, 20½-× 22-in face, 5½-in top and bottom (520 × 560 × 140 mm), 8-mil PE film, plain	0.49	1.33	0.038
Pinch-style open-mouth bag, 20 × 4 × 30¾ (510 × 100 × 780 mm), 1/10 PE 50, 2/50, 1/60 kraft, plain, no printing	0.65	2.00	0.057
Small bags, pouches, and folding boxes[h]			
Pouch, 8¾ × 16¾ in (220 × 425 mm), 2-ply PE film, 2-mil- (0.05-mm) thickness per ply	$0.13	0.12	0.0034
Bag, sugar-packet style, 6 × 2¾ × 16¾ in (150 × 70 × 425 mm), 2/40-lb basis weight, natural kraft paper	0.11	0.12	0.0034
Bag, pinch style, 8¾ × 3 × 21 in (220 × 75 × 530 mm), 2/40-lb basis weight, natural kraft paper	0.11	0.12	0.0034
Folding box, 5 × 1 × 8 in (125 × 25 × 200 mm), reverse-tuck design, 12-point kraft board with bleached white exterior	0.23	0.028	0.0008
Folding box, 9½ × 4½ × 15 in (240 × 115 × 380 mm), full-overlap top and bottom, 30-point chipboard with bleached white exterior	0.47	0.37	0.0105

For tuck-in sleeve, add $0.05/bag. Unit cost is for unprinted bag. For printing add the following up charges. U.S. dollars per 1000 bags:

1 side, 1 color, $13.50
1 side, 2 colors, $16.85
1 side, 3 colors, $22.15
2 sides, 1 color, $16.85
2 sides, 2 colors, $22.15
2 sides, 3 colors, $28.50

Polyethylene-film gauges

mil	Actual mm	Nearest mm
0.5	0.0127	0.01
1.0	0.0254	0.03
1.5	0.0381	0.04
1.75	0.0445	0.04
2.0	0.0508	0.05
8.0	0.2032	0.20

Multiwall kraft-paper basis-weight equivalents

U.S. customary, lb/3000 ft² ream	SI, g/m²
40	65
50	81
60	97

Permeability of common packaging films*

Type of film	Water-vapor transmission†	Gas permeability‡ O_2	Gas permeability‡ N_2	Gas permeability‡ CO_2	Water absorption
Cellophane, nitrocellulose-coated	0.3	1	1	13	High
Nylon	19	25	160	160	Medium
Polycarbonate	11	300	50	1000	Medium
Polyester, oriented	1.7	4	1	16	Low
Polyethylene, low-density	1.3	550	180	2900	Low
Polyethylene, high-density	0.3	600	70	4500	Low
Polypropylene	0.7	240	60	800	Low
Saran	0.2	14	12	4	Low

*From J. R. Hanlon, *Handbook of Package Engineering*, Technomic Publishing Co., Lancaster, PA 17604, 1992 ed.
†g loss, 24 h/(100 in²·mil), at 95°F, 90 percent relative humidity.
‡cc, 24 h/(100²·mil), at 77°F, 50 percent relative humidity; ASTM D1434.

TABLE 21-16 Typical 1996 Cost of Containers for Chemical Products (*Concluded*)

Container size and description	Unit cost, US$	Usable volume, ft³	Usable volume, m³
Corrugated cartons and bulk boxes[h]			
Regular slotted carton (RSC), 24 × 16 × 6 in (610 × 405 × 150 mm), 275-lb-test double wall, stapled (stitched) joint	1.25	1.33	0.038
RSC, 16 × 6 × 24 in (405 × 150 × 610 mm), 275-lb-test double wall, stitched joint, end-opening style	0.90	1.33	0.038
Bag in box, RSC, 15 × 15 × 22 in (380 × 380 × 560 mm), 275-lb-test double wall, stitched liner, 600-lb-test double wall, 6-mil (0.15-mm) PE liner	3.80	2.86	0.081
Bulk box, 600/600 (test in lb for both pieces), laminated inner lining, approximately 41 × 34 × 36 in (1040 × 865 × 915 mm); includes special wood pallet and 8-mil (0.2-mm) blown low-density PE liner	35.00	5.00	0.142
Carboys, plastic drums, jars, and bottles[h]			
Carboy, 13½ gal (51 L), PE, blow-molded	39.90	1.35	0.038
Drum, PE, 15 gal (57 L), blow-molded,	41.00	2.00	0.057
Carboy, 15 gal (57 L), glass, nitric acid service, wooden crate	128.00	2.00	0.057
Jug, 1 gal (3.78 L), glass, with finger handle, plastic 38-mm cap, with corrugated reshipper carton	3.10	0.1335	0.004
Bottle, 1 qt (0.95 L), glass, Boston round, plastic 28-mm cap	1.50	0.034	0.001
Jar, 1 qt (0.95 L), glass, wide mouth, plastic 89-mm cap	1.60	0.034	0.001
Jar, 1 qt (0.95 L), glass, plastic 63-mm cap	1.42	0.034	0.001
Jar, 1 gal (3.78 L), PE, wide mouth, plastic 100-mm cap	1.47	0.1335	0.004
Bottle, 1 gal (3.78 L), round, PE, narrow neck, plastic 38-mm cap	1.85	0.1335	0.004
Bottle, 1 qt (0.95 L), PE, narrow neck, plastic 28-mm cap	0.94	0.034	0.001
Jar, 1 pt (0.47 L), PE, wide mouth, plastic 53-mm cap	0.71	0.017	0.0005

Cost US$[h]

	Expendable grade		Warehouse reusable grade	
	9-block type	Stringer type	9-block type	Stringer type
Pallets[h]				
40 × 48 in (1015 × 1220 mm)	11.76	10.90	17.78	16.32
35 × 42 in (890 × 1065 mm)	10.17	10.17	16.49	15.17
42 × 48 in (1065 × 1220 mm)	17.40	17.40	20.10	18.51
48 × 48 in (1220 × 1220 mm)	18.81	18.81	21.69	19.97
44 × 50 in (1115 × 1270 mm)	21.45	21.45	24.53	22.60

Wrap materials	US$/lb
Film, PE, Grade ADL, blown type	1.05
Film, PE, Grade ASF (shrinkable)	1.25
Film, polypropylene, shrinkable, yield before shrinkage = 31,100 in²/(lb·mil)	3.37
Paper, kraft, wrapping quality, 50-lb/ream basis-weight yield = 3000 ft²/ream	0.50
Film, PE, stretchable type for pallet wrap, 1.5 mil × 20 in (0.04 × 510 mm) wide	1.15

[a] Drum has 2-in and ¾-in national-pipe-thread (NPT) openings in head.
[b] Truckload quantity price, FOB east-coast manufacturer's plant.
[c] DOT = U.S. Department of Transportation. Also UN (United Nations).
[d] Sequence of top, body, and bottom gauges. For example, 18-20-18 = 18-gauge top, 20-gauge body, and 18-gauge bottom.
[e] Removable head secured with bolted ring with screw draw-up.
[f] Drums are of plain fiber, have steel cover and bottom, and have lever-operated closing ring.
[g] Truckload-quantity price, FOB buyer's plant.
[h] Truckload-quantity price, FOB east-coast buyer's plant.
[i] Prices given are adequate for comparing alternatives. For budget purposes, actual, recent vendor quotation must be used due marketplace fluctuations in prices.
Explanation of U.S. DOT term:
PACKING GROUP I, II, III
P.G. I Great danger
P.G. II Medium danger
P.G. III Minor danger

Polyethylene-film* yield table

Thickness, in	Thickness, mm	Yield, in²/lb	Yield, m²/kg
0.001	0.025	30,000	19.4
0.0015	0.040	24,000	15.5
0.002	0.050	15,000	9.7
0.003	0.075	10,000	6.5
0.004	0.100	7,500	4.8
0.008	0.200	3,750	2.4
0.010	0.250	3,000	1.9

*Flat sheeting.

TABLE 21-17 Abstract of Part 172-101 of Code of Federal Regulations (CFR) Title 49 to Illustrate the Ethyl Alcohol Example in the Text. (U.S. Government Printing Office)

Symbols (1)	Hazardous materials descriptionsand proper shipping names (2)	Hazard class or Division (3)	Identification Numbers (4)	Packing group (5)	Label(s) required (if not excepted) (6)	Special provisions (7)	(8) Packaging authorizations (§ 173.***)			(9) Quantity limitations		(10) Vessel stowage requirements	
							Exceptions (8A)	Non-bulk packaging (8B)	Bulk packaging (8C)	Passenger aircraft or railcar (9A)	Cargo aircraft only (9B)	Vessel stowage (10A)	Other stowage provisions (10B)
—	Ethanol *or* Ethyl alcohol *or* Ethanol solutions *or* Ethyl alcohol solutions.	den 3	UN1170	II	FLAMMABLE LIQUID.	T1	150	202	242	5 L	60 L	A	
		—	—	III	FLAMMABLE LIQUID.	B1, T1	150	203	242	60 L	220 L	A	

TABLE 21-18 Agency and Administrative Law

Title	Symbol	Regulate or affect
International		
United Nations	UN	Packages and labeling for products moving among member nations.
Intergovernmental Maritime Consultative Organization	IMCO	
Federal		
Department of the Treasury Bureau of Alcohol, Tobacco and Firearms, Title 27	ATF	Packages and labeling for alcohols, tobacco, firearms, and explosives.
Department of Transportation Transportation Safety Act, Title 49	DOT	Packaging and labeling for all hazardous materials shipped in interstate commerce.
U.S. Coast Guard, Title 46	USCG	Set packaging, labeling, blocking, and bracing for all freight moving by United States–registry ships on lakes, rivers, or oceans.
Department of Labor Occupational Safety and Health Act, Title 29	OSHA	Package-filling and -handling machinery, workplace design, warehouse practice, and acceptability of packages from workplace and warehouse viewpoint.
Food and Drug Administration Federal Food, Drug, and Cosmetic Act, Title 21	FDA	Packages, packaging machinery, and workplace from viewpoint of their effect on food and drug purity; package labeling and marking.
Environmental Protection Agency, Title 40	EPA	Packaging facilities, packaging and labeling, package disposal, workplace refuse disposal, cleanup and disposal of spills.
Clean Air Act	CAA	
Clean Water Act	CWA	
Resource Conservation and Recovery Act	RCRA	
Federal Insecticide, Fungicide, and Rodenticide Act	FIFRA	
Toxic Substances Control Act	TSCA	
Nuclear Regulatory Commission Title 10	NRC	Packaging and labeling for nuclear materials and wastes
State		
Department of Transportation Labor Environmental Protection Agriculture Others	Example: New Jersey Department of Transportation	Packaging, labeling, workplace, packaging machinery, etc., in *intrastate* commerce. Regulations generally parallel those of federal departments but frequently have important differences and additional requirements.
City		
Departments of Health Labor Fire Protection	City fire department; example: NYFD	Packages, packaging machinery, packaging facilities, and materials which are transported, stored, and handled in the city. These local laws are in addition to the requirements of state and federal law.
Industry associations		
Air Line Pilots Association	APA	Materials which can be carried on commercial aircraft piloted by Air Line Pilots Association members.
International Air Transport Association	IATA	Materials which can be carried on members' aircraft and packaging and labeling requirements for them.
International Civil Aviation Organization	ICAO	Materials which can be carried and the packaging and labeling for them.
Association of American Railroads Bureau of Explosives	AAR B of E	Packages and loading, blocking, and bracing for all hazardous products shipped by rail in the United States. Bureau standards are generally accepted by all railroads and are the basis for R. M. Graziano's Tariff *Hazardous Materials Regulations of the Department of Transportation by Air, Rail, Highway, and Water,* latest edition.
Uniform Freight Classification Committee, Rules 40 and 41	UFC	Set packaging standards for all freight moving by *rail.*
American Bureau of Shipping National Cargo Bureau	ABS	Packaging, labeling, loading, blocking, and bracing for all freight moving by United States–registry ships on lakes, rivers, or oceans.
National Motor Freight Traffic Association National Motor Freight Classification	NMFC	Set packaging standards for all freight moving by highway.
National Fire Protection Association	NFPA	Packages, packaging facilities, and warehouse designs and operation.
Special carriers		
United Parcel Service	UPS	Packaging, labeling, and size and weight of small packages carrying hazardous materials. Requirements meet DOT standards. Quantities generally do not exceed 1 gal (3.785 L).
U.S. Postal Service	USPS	Materials which may be shipped and packaging, labeling, and size and weight of small packages handled by parcel post.
Federal Express Corp.	FEDEX	Packaging and labeling for hazardous and nonhazardous materials and products which they will carry.

TABLE 21-19 Performance Testing of Steel Drums—Type 'A' for Packaging Group II

Test	CFR 49 reference	Criteria summary
Drop test	178.603(e); (ii)	1.2 Meters (3.0 ft.)—no leakage
Leak proofness test	178.604(e); (2)	20 kPA (3.9 PSIG)—no leakage
Hydrostatic test	178.605(d); (1)	100 kPA (15 PSIG)—no leakage
Stacking test (By compression machine)	178.606(c); (2), (ii)	2000 lbs. (907 kg)—no leakage
Vibration	178.608(b), (3)	1 in. (2.54 cm) Amplitude at resonant frequency for 1 hour—no leakage

This information is taken from CFR 49, issue of October 1, 1992. The table is intended to be illustrative of the use of CFR 49. It should not be used as the basis for choosing a drum or other type package. Each package and product requires specific analysis to identify the container which meets customer needs and complies fully with U.S. DOT and UN regulations.

ethyl alcohol in part 172.101 and find that the required packaging was described in parts 173.125 and 173.119. According to Part 173.119, a 55-gallon (208 liter) steel drum was authorized for ethyl alcohol and its specifications could be found in Part 178.116. The type 17E drum was completely specified in this section. Under the new performance-oriented specification approach, the packaging requirements are specified in Part 172.101 which states that ethyl alcohol falls into the hazard described under Packing Group II, and packaging authorizations are found in Part 173.202. This shows that a Type 1A1, 55-gallon (208 liter) drum which meets standards given in Part 178.504 and performance specified in 178 subpart M can be used. Table 21-19 summarizes the test criteria. Any drum which can meet these criteria is authorized and may be used for this product. The manufacturer of the drum and the seller of the drum must warrant that the drum does meet these criteria and that either they have tested this design on a routine basis to verify that it meets these criteria, or that a third party has done so. They must be able to produce records that these test requirements have been complied with.

Under the old regulations, the marking on the bottom of the 17E drum was as shown in Fig. 21-36. Under the new regulations the marking on the bottom of the drum is as shown in Fig. 21-37. After October 1, 1994 all packages must be marked only with the new marking. Those new packages which are in the distribution system and contain the old mark may be used until October 1, 1996. After this date only packages marked with the approved UN marking are authorized by the U.S. DOT.

Also of note is a growing trend among packagers of hazardous materials to determine quantitatively the degree to which the package they will use exceeds that minimum performance requirement as specified by the U.S. DOT or UN. Using programmable shock and vibration machines and the damage-boundary-curve method, it is possible to develop the fragility of any package which then permits comparison of one alternative design with another, on a quantitative and economic basis. Rutgers, The State University of New Jersey, Center for Packaging Science and Engineering has been conducting research in this field.

Competent advice on the correct packaging to use for hazardous materials or other products is obtainable from consultants in the field of packaging who are members of the Institute of Packaging Professionals, consultants counsel. A brochure listing the qualifications of member consultants is obtainable from the IOPP.

Whatever hazardous materials are involved, whether they be new products, an existing product in a new package type, hazardous waste, or any other hazard category, the proposed packaging and all conditions which are expected to be incident to its use should be reviewed by a competent attorney who specializes in distribution and packaging matters. In the larger corporations, the law department usually has such a specialist. If not, local bar associations can provide the names of attorneys with this specialty.

It cannot be overemphasized that in the packaging of hazardous materials, extra steps and precautions must be taken to provide absolute compliance with established regulations. The penalties for failure to do this are exceedingly high, but the potential for serious injury to people and damage to the environment are of greater significance. A publication which addresses changes and issues in the packaging and shipping of hazardous materials is *HAZMAT PACKAGER AND SHIPPER* published by Packaging Research International, Inc., PO Box 3144, West Chester, PA 19381-3144, phone 610-436-8292, FAX 610-436-9422. Changes in CFR49 occur often. Before being published, they appear in the *FEDERAL REGISTER* which is published five times per week. CFR 49 is published on October 1, of each year and incorporates changes of the previous year.

Once the package alternatives permitted by government or transportation companies have been determined and marketing and production considerations are known, performance and economic evaluation must be made. This evaluation should consider packaging as part of a system. Not only must the package itself be considered, but so must factors which affect the package or are affected by it. If a choice of shipping in bulk form or in packages exists, cost comparisons must be made (Table 21-20).

Metric-system dimensions for packaging are not used extensively in the United States, but initial steps are being taken to permit use of these dimensions. The subject is under intensive study by both the packaging-supply and the packaging-using industries. SI equivalents are usually available from package suppliers, but at present all ordering in the United States is done in the U.S. customary system. Table 21-21 gives the degree of expected metric conversion. In the United States suppliers are using millimeters as the principal metric measure. When a soft conversion is made, increments of 5 mm are used. A converted package dimension is rounded up or down to the nearest multiple of 5 mm. For example, a bag-face width of 16 in equals 406.4 mm, which would be rounded down to 405 mm.

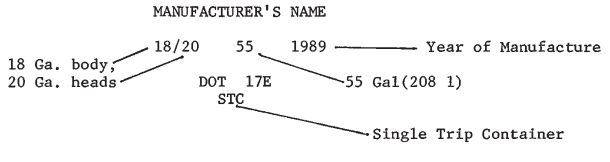


FIG. 21-36 Marking authorized by the U.S. DOT prior to October 1, 1994 prior to the change to performance-oriented specifications. Marking is found on the bottom head of the drum.

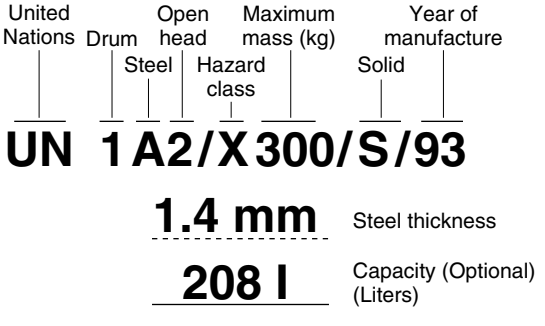


FIG. 21-37 Marking which complies with U.S. DOT and UN regulations and applies to a specific open-head steel drum. (*Courtesy of the Steel Shipping Container Institute, Union, NJ.*)

TABLE 21-20 Container Comparative Data[a]

Product: Thermoplastic pellets of 33-lb/ft^3 (528.7-kg/m^3) bulk density

Parameter	Domestic paper bag	Bulk corrugated-paper box	Intermediate bulk container	Bulk hopper truck	Ship container	Railroad hopper car	Intermediate bulk container
Construction	Multiwall pasted valve bag, 4-ply construction, with inner ply having an extrusion coating of low-density PE	Corrugated box, one-half RSC design, made of 600-lb burst-strength-test double wallboard, A-C flute laminated; includes cap, inner, and wood pallet	Flexible bag made of woven polypropylene of 2000 denier, 12 × 12 weave, with PE liner and nylon support straps	Welded-aluminum tank with pneumatic unloading pump; undercarriage equipped with pneumatic tires	Welded- or riveted-aluminum construction, with International Organization for Standardization (ISO) end castings for lifting by standard spreader	Welded-steel construction with plastic-coated interior, equipped with 100-ton trucks for 4-ft, 8½-in-gauge tracks	Rigid container made of welded-aluminum construction with butterfly discharge valve and fill port
Size	16 × 25 × 6.5 in (405 × 635 × 165 mm)	41 × 34 × 36 in (1040 × 865 × 915 mm)	53 in diameter × 53 in high (1350 × 1350 mm)	8 ft wide × 30 ft long (2.4 × 9.1 m)	8 × 8 × 35 ft (2.4 × 2.4 × 10.7 m)	5700 ft^3 (161.4 m^3)[b]	42 × 48 × 84 in (1070 × 1220 × 2135 mm)
Capacity, lb (kg)	55.1 (25)	900 (408)	2205 (1000)	42,000 (19,051)	50,000 (22,680)	180,000 (81,648)	2205 (1000)
Tare weight, lb (kg)	0.7 (0.32)	50 (22.7)	20 (9.1)	20,000 (9072)	4200 (1905)	100,000 (45,360)	255 (115.7)
Unit cost, US$	$0.55	$27.00	$59.00	$75,000	$16,000	$100,000	$2500
Lease cost, US$/month				$920	—	$685	$40[d]
Useful life	1 trip	1 trip	10 trips	15 years	5 years	25 years	10 years
Practical shipping radius, mi (km)	Any	Any	Any	250 (402) maximum	Any	300 (483) minimum	Any
Cost of typical system, US$/100 lb (45 kg)[e]	$6.81	$7.76	$5.08	$0.80	$0.80	$0.32	$4.63
Plant investment, US$ × 1000	$90–180[b]	$22–238	$27–252	$22–315	$45–315	$36–315	$27–252

[a]Based on 1996 prices.
[b]See Fig. 21-56 for typical plant layout.
[c]Mileage credit is paid to owners or lessees of this type of hopper car. To gain mileage credit car must be loaded. Rate is negotiable. A typical rate is $0.43 per loaded mile.
[d]Lease cost is based on a period equal to the useful life.
[e]Includes cost of container, filling, handling, and storage for minimum volume of 1000 tons per month (908 metric tons per month) but does not include freight or amortization of filling equipment.
[f]Represents typical investment in filling and handling equipment. Actual amount depends on plant layout and nature of existing facilities.

TABLE 21-21 Expected Metric Conversion of Packages for Chemical Products in the United States

Package type	Degree of conversion*
Bags (paper, plastic)	Hard
Boxes (paper)	Hard
Drums (fiber)	Hard
Drums (steel)	Soft
Pails (steel, plastic)	Soft
Cans (steel, fiber)	Hard
Bottles (glass, plastic)	Hard
Paper (kraft)	Hard

*Hard conversion: resized package dimensions to hold the nearest acceptable metric unit. Example: 50-lb (22.7-kg) multiwall paper bag changed to hold 25 kg (55.1 lb). Size can be limited by the maximum-size package available.

Soft conversion: the volume of the package is unchanged, and its metric equivalent is stated. Example: 55-gal drum equals 208 L.

For kraft paper, conversion will eventually be a hard conversion to two basis weights of 75 and 90 g/m^2, which will replace the 40-, 50-, and 60-lb basis weight currently used.

Package development involves the design, specification, and testing of packages. Sophistication of chemical and pharmaceutical industry products sold to industry and consumers is increasing. Package design takes into account four principal considerations. First is the preference of the customer for a particular type of package and whose preference is often opposed to that of the producer of the product. Second is compliance with applicable regulations. Third is the effect which a package choice will have on production-plant-operating conditions. A fourth consideration is the effect of atmospheric gases on the product itself, especially when the product is packaged in other than metal or glass. Of concern are water vapor, oxygen, and carbon dioxide, which can permeate most flexible package materials. There are thermoplastic films available that offer barrier properties which restrict atmospheric gases from entering a package. Additionally, the thermoplastic films can be combined with aluminum foil to produce impermeance. Aluminum foil has the propensity to stress crack when used in flexible packages. To overcome this problem the film industry has devised a method of depositing vaporized aluminum directly onto a thermoplastic film. This notably improves its permeation properties. Table 21-16 lists some of the common thermoplastic films and their barrier properties. Where pharmaceutical products are involved, and this would also include intermediate chemicals used in their formulation, the FDA requires that any reactions between the packaging material and the product itself must be known and often this must be reported in parts per million or finer. CFR 29, Part 1200 gives this for many types of packaging materials and containers.

Package testing is manditory for chemical products which are deemed as hazardous, as set forth in CFR 49, Part 172.101. A package for hazardous material being offered by a supplier must be tested by them or by a qualified third party. The tester must certify that the package complies with the DOT regulations and the design has been tested satisfactorily for a given packing group. The purchaser does not have to be concerned with the testing itself but only that it has been done and that the supplier can certify that the package has passed the required tests.

A second type of tests are those which shippers require when using a new package never before used for a given product, or an improved existing one. This type of testing is done in a simulated distribution environment using the actual package and often the product which is involved. The expected shock, vibration, compression, and impact shock which might be encountered in a distribution environment can be simulated in the laboratory, and a fair assessment made of the ability of the package to withstand or exceed expected conditions. One test protocol which accomplishes this is that published by the American Society for Testing Materials (ASTM) No. D4169. This protocol allows the user to define the shipping environment in minute detail, to carry out tests which simulate shock, vibration, compression, etc., and then to appraise the results of these tests. Copies of this test protocol may be obtained from ASTM, 1916 Race Street, Philadelphia, PA 19102.

Another test protocol is that specified by the International Safe Transit Association (ISTA), East Lansing, Michigan. This also simulates transportation and handling conditions. Transportation companies—truck, rail—accept ISTA test results and will transport packages bearing the ISTA marks.

Competent testing laboratories which can provide tests according to the ASTM D1469, ISTA, DOT, UN, and other protocols are located strategically throughout the United States and in most of the developed nations. The yellow pages of the telephone directory are useful to find such laboratories.

LIQUID PACKAGING

Containers Containers for liquids consist principally of drums, pails, and cans made of steel or plastic and of bottles and vials made of plastic or glass. The chemical industry is often involved with all these containers, but the most frequently used packages for industrial chemicals are steel drums and pails. For exotic products, stainless-steel drums and pails are available. The most common types used are 208-L (55-gal) drums and 19-L (5-gal) pails.

Once the appropriate package has been determined by consulting governmental and carrier regulations, the type of material compatible with the product needs to be determined. A wide variety of coatings is available for lining carbon steel drums and pails. Suppliers are often able on the basis of experience to assist in determining a lining which will be compatible with the product. When prior information is unavailable, laboratory tests can determine compatibility. Laboratory tests are often desirable before field trials. In some instances, a product may not be compatible with metal. This circumstance has led to an important container, the **all-plastic 208-L (55-gal) drum.** Made from blow-molded high-density polyethylene, this container is especially useful for products which might react with carbon steel or whose value does not warrant stainless steel. Special treatments are available to make the inner surface of the plastic drum impervious to penetration of many products. Sulfonation and fluorination are prominent among these processes.

Two basic designs of steel drums and pails exist: the tight-head and the open-head. Tight-head drums have both top and bottom members permanently fastened to the drum body. Open-head drums have only the bottom permanently attached. As the term "open-head" implies, the top of the drum does not have a permanently fixed cover; rather, a removable head is used. This head is designed so that a locking ring secures it to the drum body. Open-head drums and pails are usually employed for viscous products or for mixtures and slurries which are difficult to pump through lines 50 mm (2 in) or smaller. Tight-head drums and pails are used for low-viscosity products. No set rule can be given for the viscosities above which an open-head drum or pail must be used.

Reconditioned and remanufactured drums are authorized by the U.S. DOT for certain hazardous materials. CFR 49 paragraph 173.28 provides details of the reconditioning process. This consists essentially of rinsing the inside of the drum, removing any dents which deform the chime, grit blasting the exterior to remove all previous labels and paint, and then recoating with a new outer finish paint. The reconditioner must put their company mark on the drum. Reconditioned drums costs 50 to 70 percent of the price of a new drum and as such are useful for packaging marginally profitable products. The regulations set forth by the U.S. DOT must be complied with in complete detail.

Remanufactured drums are also permitted. Remanufacturing involves the dismantling of the drum, usually involving removal of the top and bottom head. All dents, rust, and other corrosion are removed by the grit blasting. New heads are then flanged onto the drum. An interior coating is given the drum when required, and the outside is painted. The drum remanufacturer must put their company mark on the drum. Remanufactured drums must withstand the same tests as a new drum. Details of DOT requirements for remanufactured drums are contained in CFR 49 paragraph 178.16. For products which are not classified as hazardous, the DOT and UN regulations do not apply but they are useful in setting a minimum performance standard for the packaging of any nonhazardous material.

Closures for drums and pails need to be determined together with the gasket material to be used. Consideration must be given to compatibility with the product and to the vibration which the container will encounter during transportation. The torque required to produce closure integrity is thus a significant factor. The typical closure sizes used in United States practice for tight-head drums are a 2-in national pipe thread (NPT) and a ¾-in NPT in the top head. For open-head drums, market considerations determine whether or not these fittings are used.

Steel drums are an ideal package because they can be stored out-of-doors and are generally impervious to weather conditions. Because of the drum's top head being recessed into the drum body, water can accumulate following a rain storm. While rusting of the drum head is undesirable a greater problem is the obliteration of whatever printing and labeling is on the drum head. To overcome this problem a patented wicking device "Drumwic" is available from Lee Technology Inc., Huntington, West Virginia. It is a low-cost way for quick removal of any accumulated water. The device is reusable. An illustration is contained in Fig. 21-40(*o*).

Tamper-evident seals and closures are commonly added to all packages. For certain products, child resistant closures are also added. There are several types of tamper-evident closures of which three are most common to liquid chemical products. First is a metal enclosure which covers the drum bung and which is crimped to it. The pulling of a tab breaks the tampered-evident enclosure which cannot be used again. It is customary to have the tamper-evident seal on both drum bungs. This holds also for pails. For small glass or plastic packages a seal is fitted into the cap which is then heat sealed to the bottle by means of an induction sealer. The construction of this seal consists of an outer layer of a thermoplastic material such as polyethylene, followed by aluminum foil, followed by a bleached kraft paper. The induction sealer induces eddy currents in the aluminum foil which raises its temperature to above the melting point of the polyethylene. The polyethylene melt then fuses the seal to the bottle. Another type also used for plastic and glass bottles is an external sleeve of shrinkable PVC (polyvinylchloride). This is usually applied by machine as the bottles move down the packaging line after being capped. They pass through a heated tunnel which raises the temperature of the seal to where it shrinks tightly around the closure, thereby providing tamper evidence. Child-resistant closures are those which are designed to be sufficiently complicated that the hand-eye coordination of the child is inadequate to open the package.

Filling Line Among filling-line considerations are filling and weighing equipment, mechanical handling of empty and filled drums, loading of filled drums onto transportation vehicles, workstation design for the safe and efficient use of personnel, and conformance to Occupational Safety and Health Administration (OSHA) and other codes. A typical drum-filling line, capable of handling two drums per minute, is shown in Fig. 21-38.

Filling and Weighing of Drums This procedure is divided into two parts: delivery of the liquid to the drum and weighing out the desired amount. Pumping the liquid product through a series of delivery pipes to the drum-filling point should follow good practice whereby reasonable velocities and pressure losses are maintained. The terminal point of the filling line is a control valve which is activated by a signal from a weight-sensing unit or scale. Valves may be pneumatically, hydraulically, or electrically operated, their operation being actuated either by an electric or pneumatic system or manually. The filling nozzle may be either top-fill or bottom-fill. Top filling is usually employed for most products, especially viscous materials or slurries. Bottom filling is used for low-viscosity products, for those having flash points under 37.8°C (100°F), or for places where static electricity is a concern. Also, products which tend to foam are bottom-filled. With a bottom-fill installation sufficient headroom is needed to permit the filling nozzle to be withdrawn from the drum. With both types of filling nozzles, a provision must be made for collecting product which dribbles from the end of the nozzle after filling is complete.

Weighing The weighing apparatus can be as simple as a platform scale in which the operator shuts off the filling nozzle when the desired weight has been reached. Automatic weighing can employ a load-cell system activating the flow-cutoff mechanism through a microprocessor. The same principles of filling and weighing as were described in the subsection "Weighing of Bulk Solids" hold for liquids. The advent of the microprocessor, image recognition, and stepper motor controls together with precision weight sensing has led to a custom-made system which can fill any drum or pail from 5 gal (19 L) to 55 gal (208 L) in sequence without the operator having to insert the fill nozzle into each container. (See Fig. 21-39.)

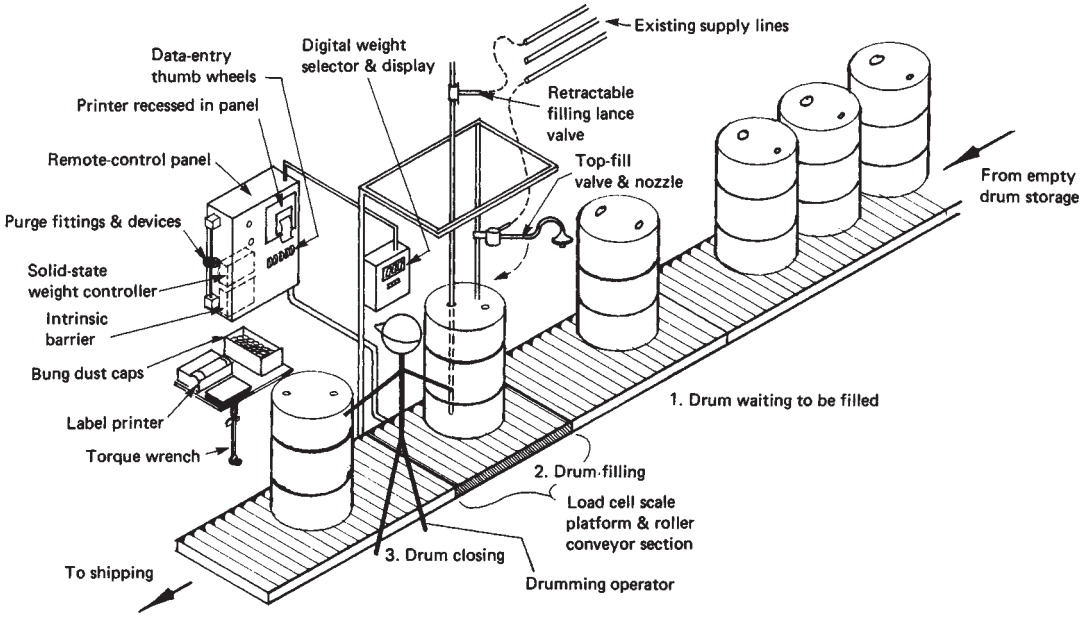


FIG. 21-38 Typical high-precision liquid filling and weighing system for packaging 208-L (55-gal) steel drums and similar smaller containers. (*Courtesy of H. F. Henderson Industries, Inc., Caldwell, NJ.*)

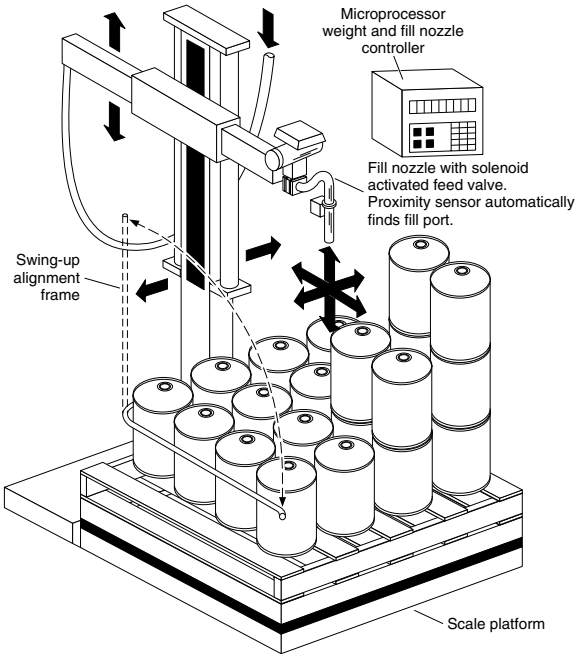


FIG. 21-39 Microprocessor-controlled drum and pail filling and weighing machine. Will fill drums or pails on one tier without operator intervention. (*Courtesy of Kg Systems, Inc., Bloomfield, NJ.*)

Work-Station Design Critical consideration must be given to the design of work stations so that filling operators work in a safe environment and are used productively. Methods design, time studies, and predetermined work-element data are helpful in determining the amount of work involved and the proper sequence of operations to permit good productivity. Of special importance (and often overlooked) is having the operator perform service functions on a drum while another drum is being filled. This is especially significant with an automatic system which does not require operator attention. The following activities can often be undertaken while a drum is being filled: removing closure plugs from the empty drum which will be filled next; replacing and tightening the closures in the drum which preceded the drum being filled; labeling and marking code numbers on the drum; and starting the filled, sealed, and labeled drum down the handling system leading to storage or transportation.

Safety Regulations Consideration must be given to safety regulations for the electrical grounding of the drum during filling, the handling of product vapors, the handling of possible inadvertent spills and splashes of product, and the design of the work station to conform to OSHA and state and local codes. Operators must be protected from contact with the product, and their physical movements must not be such as could cause potential injury. Work-station design benefits from consultation with governmental bodies and with equipment vendors and consultants.

Small Liquid Packages The packaging of small packages of liquids is a specialized field. High-speed bottle and can fillers typically are of volumetric rather than weigh design. Up to a size of 3.8 L (1 gal) volumetric fillers are used almost universally when the filling rate exceeds 10 containers per minute. Below this rate, filling is controlled by weight or even volumetrically by an operator activating manual controls.

SOLIDS PACKAGING

Containers for solids include bags, bulk boxes, cartons, and drums. While the intermediate flexible bulk container (IBC) has become an important package of world commerce, the most used package remains the multiwall paper bag, supplemented by bags of similar design made of plastic film or plastic woven mesh.

Multiwall Paper Bags These bags (Fig. 21-40), made from plies of kraft paper or from combinations of kraft and special-purpose papers and plastics, are the most common packages for almost any pelleted or powdered material as well as for briquettes or bats of such solids as synthetic rubber, waxes, and insulation.

Empty bags are ordinarily shipped compressed (to obtain high load density) and on pallets, the most common of which measure 1220 by 1065 mm (48 by 42 in), 1220 by 1015 mm (48 by 40 in), and 1270 by 1115 mm (50 by 44 in). The number of empty bags per pallet varies with size, 1500 to 2000 being common. A typical filled pallet weighs about 907 kg (2000 lb). Pallet loads are often triple-tiered in warehouses.

Two bag designs are common: the **valve** and the **open-mouth** types. The **valve** bag has both ends closed during fabrication, filling being accomplished through a small opening (valve) in one corner of the bag. The open-mouth bag has one end closed at the factory and the other after filling.

Most **open-mouth bags** are closed by sewing, whereas adhesive is used for the pinch type. The pinch bag has been the subject of inten-

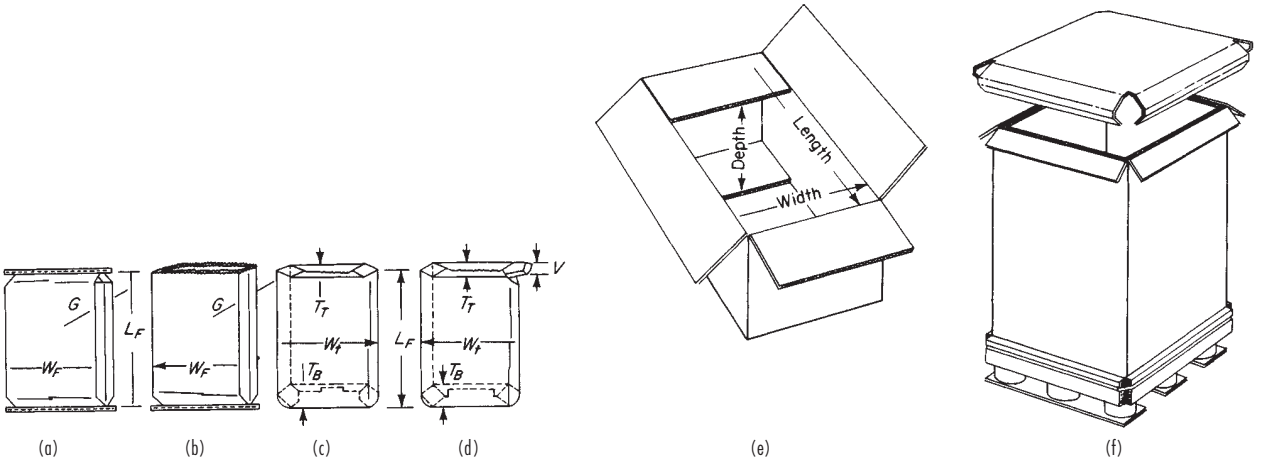


FIG. 21-40 Typical packages used for chemical products. (*a*) Sewn valve bag. (*b*) Sewn open-mouth bag; pinch-bottom-type open-mouth bag. (*c*) Pasted valve bag. (*d*) Pasted valve tuck-in-sleeve bag. (*e*) Principal (inside) dimensions of a regular slotted carton (RSC). (*f*) Bulk box of corrugated fiberboard for product weighing 450 kg (990 lb).

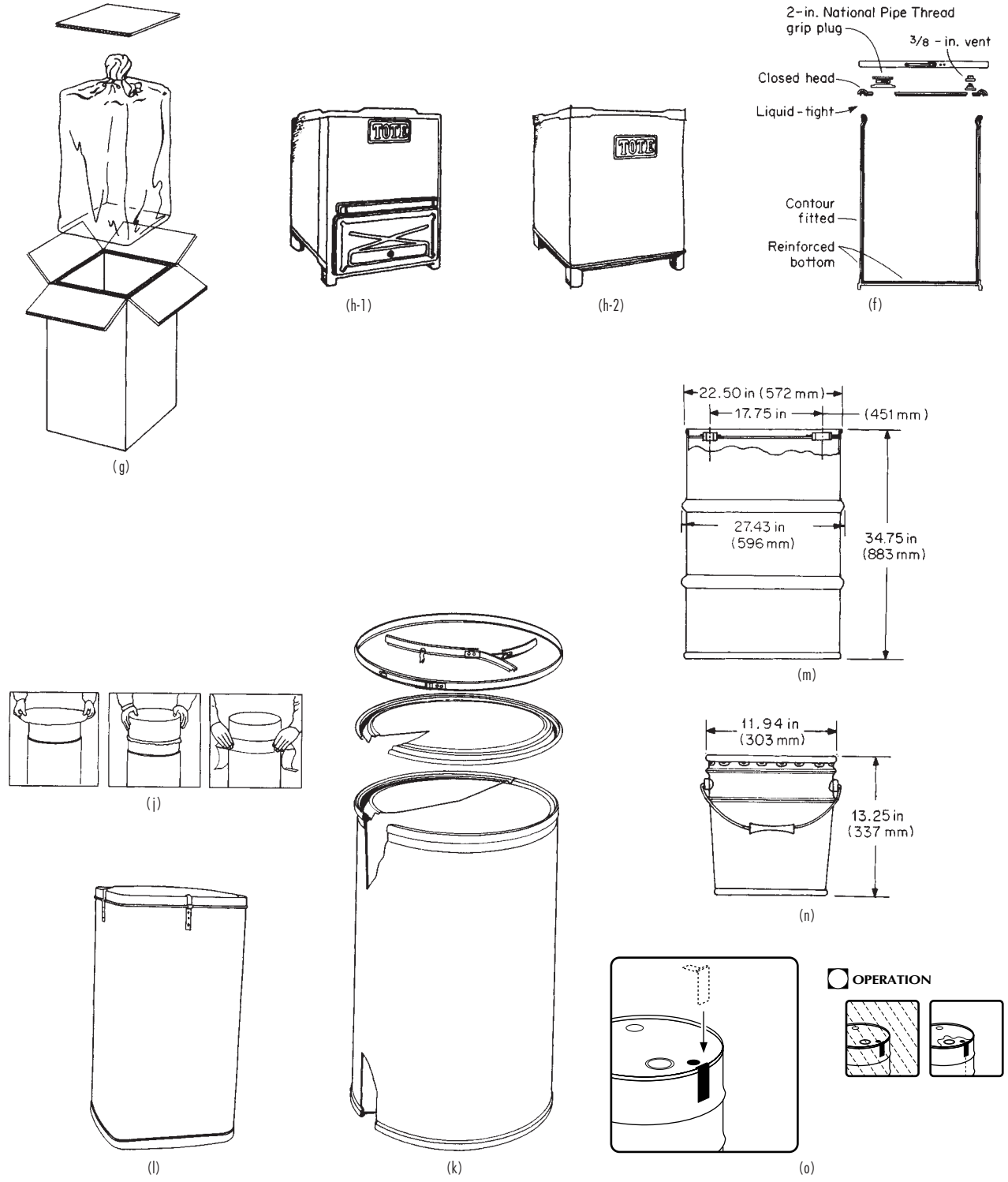


FIG. 21-40 (*Continued*) Typical packages used for chemical products. (*g*) Bag in box. (*h*) Tote-bin rigid intermediate bulk container: 1—for solids, 2—for liquids. (*Courtesy of Hoover Universal, Inc., Materials Handling Division.*) (*i*) Liquid-type polyethylene drum with fiber overpack. (*j*) All-fiber drum with removal top. (*k*) Lever-locking fiber drum. (*l*) Ro-Con rectangular fiber drum; clip-mounted top. (*Courtesy of Greif Bros. Corp.*) (*m*) 208-L (55-gal) DOT Packing Group II closed-head steel drum. (*n*) 19-L (5-gal) DOT Packing Group III open-head universal steel pail with lug-type cover. (*o*) DRUMWIC™ device for removal of water from drum heads stored out-of-doors. U.S. Patent No. 5,373,962. (From *Lee Technologies, Inc. Huntington, WV.*)

sive development by the bag industry, and as a result it has substantially displaced the sewn open-mouth bag and to some extent, valve bags. Reasons for this change include the ease, reliability, and repeatability of closing (sealing) equipment as well as the close control of the sealing adhesive applied by the bagmaker. The preapplied adhesive is activated by the closing machine in the user's plant. The positive closure of the pinch bag produces a container which completely seals in the product. Valve bags can also be sealed if they are provided with sealable sleeves. An advantage of valve bags over the open-mouth type is the availability of highly productive filling machines that not only require less labor than open-mouth filling equipment but also are capable of higher packing rates. In addition, the sealed valve bag permits the greatest pallet-load density. Bags may be fabricated from a variety of readily available flexible materials. In addition to kraft paper, barrier materials are available to prevent moisture or gases from entering or leaving the bag. These range in permeability from polyethylenes to aluminum foil. Table 21-16 presents some of the more prominent moisture barriers and their typical properties.

In the interest of standardization, the Institute of Packaging Professionals Chemical Packaging Committee (formerly the Chemical Manufacturers Association Packaging Committee) recommends four sizes of expendable four-way-entry pallets for bagged chemicals given in Table 21-22. The most common pattern consists of five bags on a 1220- by 1065-mm (48- by 42-in) pallet. This pallet size permits maximum trailer loading.

TABLE 21-22 Preferred Bag-Pallet Sizes*

Pallet size		Filled-bag face width		Filled-bag face length		Bags per tier (pattern)
in	mm	in	mm	in	mm	
48 × 40	1220 × 1015†	16	405	24	610	5
48 × 42	1220 × 1065	16	405	24	610	5
52 × 44	1320 × 1115	17.25	440	26	660	5
52 × 36	1320 × 915	16	405	36	915	3

*From Institute of Packaging Professionals Chemical Packaging Committee.
†Also GMA (Grocery Manufacturers Association) and ISO standard.

Sewn valve bags and sewn open-mouth bags are less important, except possibly for products with densities over 960 kg/m^3 (60 lb/ft^3) or for individual or small-lot shipments. These bag designs have the advantage of providing an easy grasp of the bag at the end of the sewing line without allowing fine powders to sift through the closure.

Valve bags usually rely on a labyrinth of paper or plastic film to seal off the valve. The automatic internal valve, while adequately protecting the contents of the bag, does allow a small amount of sifting of fine powders.

The starting point in bag-size determination is the weight or volume of product to be packaged and its bulk density (aerated and settled). Also to be considered are particle size, shape, and weight; degree of aeration at time of packaging; flow characteristics; temperature and relative humidity; type of handling system up to and including the filling machine; bag-closing method; bag style; and pallet size and pattern. Three sets of dimensions are needed: (1) **tube**—outside length and width of tube before bag closures are fabricated; (2) **finished face**—length, width, and thickness of bag after fabrication; (3) **filled face**—length, width, and thickness of bag after filling. Table 21-23 and Fig. 21-40 show these dimensions and their interrelations.

A first approximation of size can be determined from Fig. 21-41, which applies to sewn valve, sewn open-mouth, pinch-type open-mouth, and pasted valve bags. The resulting tube width and length can then be converted into finished and filled dimensions, and bag samples ordered for field verification. Changing bag size to accommodate different weights, density variations, pallet patterns, etc., becomes a simple matter through the use of the graph. Correction factors for particular situations such as special plies, type of filling machine, storage system, and product characteristics are given in Table 21-24.

To use the graph, given the weight of material to be packed, follow these steps: (1) obtain the settled and loose (or aerated) bulk densities of the product (a 1-ft^3 box serves this purpose well), and then calculate the average of the two densities; (2) calculate the bag-volume requirement from the relation $V_b = [W \text{ lb (weight to be packed)} \cdot 1728]\, d \text{ lb/ft}^3$ (average density); (3) multiply V_b by the product of the correction factors (Table 21-24), which reflect product, storage, and packaging conditions; (4) from Fig. 21-41 obtain the bag-tube equivalent T_e; and (5) using the corrected V_b, determine the bag size needed for palletizing.

Example 1: Determination of Proper Bag Size 55.1 lb (25 kg) of plastic pellets having a bulk density of 38.5 lb/ft^3 (615 kg/m^3) are to be packaged in pasted valve bags constructed of three kraft plies and a free polyethylene (PE) 2-mil (0.05-mm) liner. Bags will be palletized in a 5-bag pattern, 40 bags per pallet, on 48- by 40-in (1220- by 1016-mm) pallets. Filled bags are permitted to overhang the pallet by 0.5 in (15 mm). Determine the proper bag size.

$$\text{Density} = 38.5 \text{ lb/ft}^3$$

$$V_b = (50/35) \times 1728 = 2470$$

Correction factor (from Table 21-24):	
For barrier sheet of 2-mil polyethylene film	1.05
For filling machine, fluidizing type	1.02
For ⅛-in- (3.2-mm-) particle-size pellets	1.00
For storage and handling 24 h	1.00
Overall correction factor (product of above)	1.07

$$\text{Corrected } V_b = 2470 \times 1.07 = 2650$$

$$T_e \text{ (from Fig. 21-41)} = 640$$

For first approximation let $T_T = T_B = 6$ in, and $L_f = 24 - 1 = 23$ in.

Since
$$L_f = L_t - (T_T + T_B)/2 - 1$$
$$L_t = 23 + 6 + 1 = 30 \text{ in}$$

and
$$T_e = W_t L_t = 640$$
$$W_t = 640/L_t = 640/30 = 21.3 \text{ in}$$

TABLE 21-23 Multiwall-Paper-Bag Dimensions

Bag type	Tube dimensions	Finished-face dimensions	Filled-face dimensions*	Valve dimensions
Sewn open-mouth	Width = $W_t = W_f + G_f$ Length = $L_t = L_f$	Width = $W_f = W_t - G_f$ Length = $L_f = L_t$ Gusset = G_f	Width = $W_F = W_f + ½$ in. Length = $L_F = L_f - 0.67\, G_f$ Thickness = $G_F = G_f + ½$ in.	
Sewn valve	Width = $W_t = W_f + G_f$ Length = $L_t = L_f$	Width = $W_f = W_t - G_f$ Length = $L_f = L_t$ Gusset = G_f	Width = $W_F = W_f + 1$ in. Length = $L_F = L_f - 0.67\, G_f$ Thickness = $G_F = G_f + 1$ in.	Width = $V = G_f \pm ½$ in. †
Pasted valve	Width = $W_t = W_f$ Length = L_t	Width = $W_f = W_t$ Length = $L_f = L_t - (T_T + T_B)/2 - 1$ Thickness at top = T_T‡ Thickness at bottom = T_B‡	Width = $W_F = W_f - T_T + 1$ in. Length = $L_F = L_f - T_T + 1$ in. Thickness = $T_F = T_T + ½$ in.	Width = $V = T_T$ +0 in. −1 in. §

Meaning of subscripts: B = bottom; f = finished-face; F = filled-face; t = tube; T = top.
*Formulas are based on conditions of bags after mechanical flattening.
†Valve dimension is flat width, which must not exceed ±½ in. + G to maintain good closure. Circumference of valve = twice the width.
‡T_T and T_B are usually equal; if they differ, use average. T = thickness.
§Valve dimension is flat width. Valve width can be made less than top width without affecting closure properties.

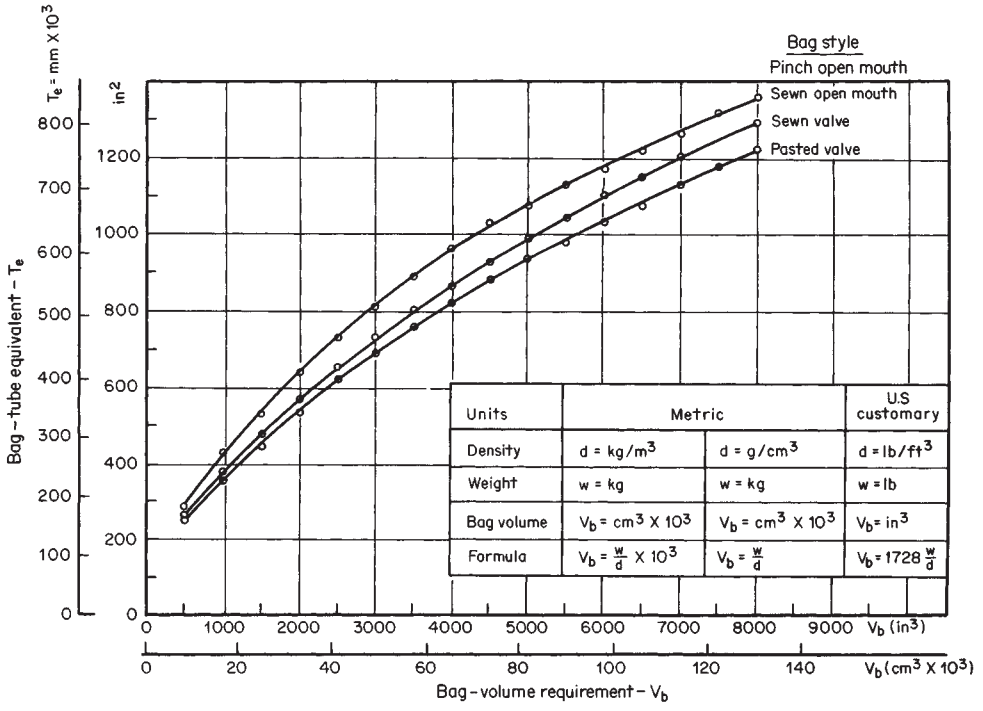
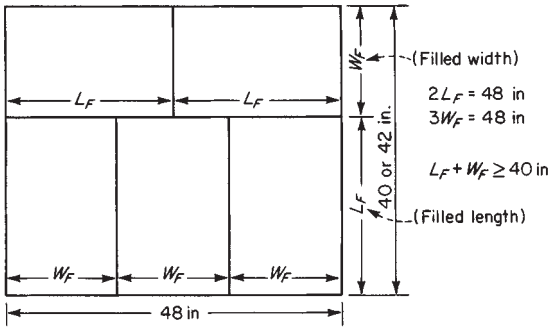


FIG. 21-41 Multiwall-bag-sizing graph. (*Raymus Associates, Inc.*)

TABLE 21-24 Bag-Volume-Equivalent (BVE) Correction Factors *f* for Specific Conditions*

Barrier and type of bag construction material		Filling-machine characteristic		Conveying, handling, and storage conditions					
						Mechanical conveying		Pneumatic conveying	
				Material particle characteristic		Off-product stream	From storage	Off-product stream	From storage
Type of material†	*f*	Type	*f*	Size, in.	Shape	*f*	*f*	*f*	*f*
Asphalt-kraft laminates	1.03	Auger, gross weigh	1.00	1/16	Pellets, round	1.00	1.00	1.00	1.00
				1/8, 3/16	Pellets, round	1.00	1.00	1.00	1.00
Polyethylene extrusion-coated on kraft	1.05	Auger, net weigh	1.03	1/8, 1/4	Cubes	1.01	1.01	1.01	1.01
Polyethylene, extrusion-coated on kraft with random partial perforations°	1.01	Belt	1.05	+200 mesh	Granules, sharp edges	1.02	1.01	1.03	1.02
		Preweigh-belt	1.01	+200 mesh	Granules, smooth edges	1.02	1.02	1.03	1.03
Polyethylene-aluminum foil-kraft laminate	1.15	Fluidizing	1.02	–50, +200 mesh	Platelets (tiny flakes)	1.03	1.02	1.05	1.03
Wax-coated kraft	1.09	Gravity	1.15	+1/4, –3/8	Flakes	1.02		1.03	
Glassine	1.04	Preweigh open-mouth	1.00						
Free polyethylene film 1 to 4 mils thickness	1.03	Gross-weigh open-mouth	1.10	–30 to +200 mesh mix	Granules, sharp	1.01	1.01	1.03	1.02
Polyethylene-film bag (extruded tubular film with heat-sealed ends)	1.10 to 1.15			–30 to +200 mesh mix	Granules, round	1.02	1.02	1.05	1.03
				–325 mesh	Granules, platelets	1.04	1.03	1.07	1.03

NOTE: Refer to Table 21-6 for metric particle sizes.
°Approximate factors are based on many observations of each material or condition stated.
†Applies to all commercially available materials of designated type, unless noted otherwise.



Since $W_F = W_f - T_T + 1$, and $W_t = W_f$

then $W_F = 21.3 - 6 + 1 = 16.3$ in

Checking for pallet-length conformity,

$2L_F = 48$ in, or $2(24) = 48$ in

$3W_F = 48$ in, or $3(16.3) = 48.9$ in

Checking for pallet-width conformity,

$W_F + L_F \geq 40$ in

or $16.3 + 24 = 40.3$ in

Summary:

Bag size: 21½ in (face width) × 23 in (face length) × 6 in top and bottom (545 × 585 × 150 mm).

Pallet size: Use 48 in × 40 in (1220 × 1015 mm).

Overall filled pallet dimensions: 48.9 × 40.3 in (1242 × 1024 mm).

This example can also be carried out in the SI system by using Fig. 21-41

Liners At the time of setup of filling, many containers for bulk solids are lined with a polyethylene (PE)-film bag, the purpose being to prevent sifting of fine particles, retard moisture pickup or release, or prevent product contamination by the construction material of the container. Liner length should be sufficient to permit the top to be closed by heat sealing or wire tying. The film gauge (thickness) needed depends on the weight, bulk density, and particle roughness of the contents. Gauges of 0.05 to 0.25 mm (2 to 10 mils) are common. For ease of placing the liner in the carton, the gusseted type is preferred; and for convenience in handling, liners are usually made as continuous tubes, with heat seals and tear-off perforations at intervals equal to one bag length (see Table 21-17 for costs).

Form-Fill-Seal, Small Bags and Pouches, and Baler Bags Product weights from a few grams to 11 kg (25 lb) are often placed in packages made of plastic film, paper, or combinations of these. Groups of packages are then shipped in cartons or baler bags (see Table 21-17 for costs).

Form-fill-seal is a machine process that forms a tube from plastic-coated paper stock, heat-seals one end, fills the resultant bag, heat-seals the other end, and then cuts off the filled bag. This method has the advantage over filling small bags or pouches in that the cost of package fabrication is avoided until the package is actually needed; packaging labor is reduced to one attendant who can service a number of machines. Also, order lead time is shortened because standard, merchant plastic film or paper can be bought from local stock, often avoiding waits of 4 to 8 weeks for fabricated bags. Offsetting this is the higher investment in equipment and the service and maintenance problems associated with automatic equipment.

Small bags and pouches are made from one or more plies of paper or plastic film. The two main types of paper bags are the satchel-bottom and the pinch-bottom. Both types usually have a gusset that helps form a rectangular cross section (a useful trait when packing in cartons or baler bags). Although order lead time is longer than for form-fill-seal and operating labor is greater, capital and maintenance costs are smaller (Table 21-17), and equipment reliability is greater. These small packages require a master shipping container. Corrugated cartons are used extensively, as is the flexible baler bag.

Baler bags are pasted open-mouth bags with one or more plies and of either satchel-bottom or self-opening (gusseted) design. Pouches are loaded into the baler with their long axis parallel to that of the baler. Since the pouches must be tightly packed, mechanical-compression loading equipment is mandatory.

Rigid Intermediate Bulk Containers Rigid IBCs are made of metal or plastic suitable for the product and service intended. Sizes available range from 0.17 m^3 (6 ft^3) to 2.83 m^3 (100 ft^3). This type of container is intended for reuse and a useful life of up to 20 years. Important economic considerations are the cost of returning the empty container to the filling location and the cleaning, handling, and storage of it. Figure 21-40 (h-1, h-2) illustrates a metal container. Table 21-20 gives economic information comparing this type of container with other containers of larger or smaller volume.

Flexible Intermediate Bulk Containers These containers are an important development of the 1970s. Made from woven polyolefins or other materials, flexible IBCs are available in a wide variety of volumes and can handle up to 1800 kg (4000 lb), depending on construction. This type of container can be equipped with a thermoplastic liner when it is necessary to protect the product against moisture or other contamination. Handling is accomplished by forklift truck or by hoist. Filling and weighing of flexible IBCs can be accomplished on specially designed weigh scales or volumetrically if the container is weighed at a remote location after filling and that weight is used as a basis for invoicing. Filling is carried out through a flexible port at the top of the container, while unloading is accomplished through a similar flexible member at the bottom. Table 21-25 gives dimensional and volumetric data. Figure 21-42 shows typical container designs and types of loading and discharge spouts.

Boxes **Bulk boxes** (Fig. 21-40) of corrugated kraft paper for dry bulk products fall into two broad categories: large, for 0.5- to 2-ton loads, and small, for loads of 23 to 68 kg (50 to 150 lb). Large boxes are used extensively for resin shipment; small ones, for certain regulated materials (such as caustic soda) and for low-bulk-density products that are assessed excessive freight rates if packed in drums.

A bulk box, sometimes called *bag in box,* consists of a box within a box plus other elements such as end pads, PE bag liners, and closing materials (tape, glue, staples). The double-wall corrugated kraft board consists of an outside liner, a corrugating medium, a center liner, another corrugating medium, and an inside liner; the single-wall board

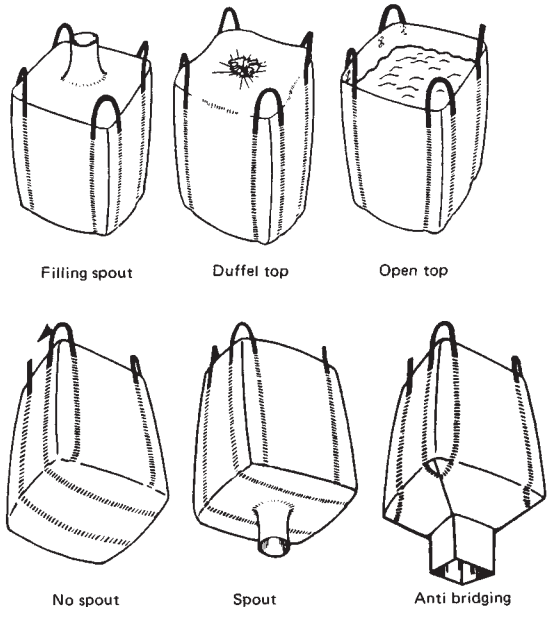


FIG. 21-42 Typical flexible-bulk-container designs and loading- and unloading-spout designs. (*Courtesy of Bonar Co., Ltd.*)

TABLE 21-25 Flexible-Type Intermediate Bulk Containers: Dimension and Capacity Data (Variable Data)*

Height		Usable volume		Maximum bulk density	
mm	in	m^3	ft^3	kg/m^3	lb/ft^3
800	31.5	0.7	24.6	1445	90
915	36.0	0.8	28.1	1250	78
1040	41.0	0.9	31.7	1120	70
1145	45.0	1.0	35.3	995	62
1270	50.0	1.1	38.3	930	58
1385	54.5	1.2	42.4	835	52
1500	59.0	1.3	45.9	770	48
1600	63.0	1.4	49.4	720	45

*From Bonar Co., Ltd.

NOTE: Maximum weight, 1 metric ton (2205 lb); cross-section dimensions, 890 by 890 mm (35 by 35 in); tare weight, 3 kg (7 lb); material of construction, woven polypropylene body and polyester lifting straps.

consists of an inner and outer liner with a corrugating medium center. The specifications for each depend on service requirements; 4100 kPa (600 lbf/in^2) burst strength is common for 454-kg (1000-lb) loads; 1900 kPa (275 lbf/in^2), for 68-kg (150-lb) loads. Materials of construction that resist high humidity and wetting with water are available.

Advantages of this container are its reclosing feature and its efficient use of storage and shipping space. Disadvantages are the space required to store box components before assembly and the limited reuse market. The lead time for ordering made-to-order boxes ranges from 3 to 6 weeks. Filling equipment is similar to that for drums. Setting up the box can require two persons because of the unwieldiness of the components. Table 21-26 gives an idea of filling speeds for several types of filling arrangements and box styles.

Wire-bound wood boxes (typical loads, 1 to 2 tons) have limited use for chemical products. The box body, consisting of thin wooden slats held in place by steel wire twisted around each slat, is fastened to a solid-deck wood pallet. The top also consists of wire-bound wooden pieces. A PE liner protects the product and prevents it from falling through the slats. Disadvantages of the container are the labor needed for setup and the space required for knocked-down boxes. Since manufacturers are usually near sources of hardwood, shipping costs to users may be high; lead times of 3 to 4 weeks are common.

Folding boxes made from chipboard are used for consumer-size units [from a few grams or ounces to about 11 kg (25 lb)] of such products as insecticides, snow-melting compounds, salt, and food additives. PE liners are often included to protect the product from moisture or to prevent it from sifting through minute openings in the top and bottom folds. Order lead time is 6 to 8 weeks. Knocked-down folding boxes are dense and store efficiently when palletized. A typical pallet measures 760 by 915 mm (30 by 36 in) with the load 1220 mm (48 in) high. Filling equipment, which can also be used for filling pouches, small bags, and glass jars, ranges from small, manually operated units to high-production, fully automatic units. Most common is the manually operated gross-weigher type.

Shipping cartons for liquids in cans and bottles, bulk solids in jars, pouches, and folding boxes, and briquetted items with or without individual packaging are usually made of corrugated kraft paper. The most common styles are the regular slotted carton (RSC), the end-opening RSC, and the center special-full overlap slotted container (SFF). End joints may be stapled, stitched, glued, or taped.

Specifications include dimensions of length, width, and depth, in that order (Fig. 21-40*e*). When boxes are set up and closed by automatic equipment, dimensional tolerances become critical. Cartons are shipped knocked down to the user from plants located in all industrial centers. Because order lead time is 4 to 6 weeks, inventories of empty boxes require considerable space. A useful booklet describing all aspects of corrugated box designs and materials is the *Fiber Box Handbook* available from The Fiber Box Association, 2850 Gulf Road, Rolling Meadows, IL 60008.

Often, the size of items packaged in corrugated cartons either does not permit interlocking of layers of cartons, or leaves considerable void space between them. Since calculating by hand the best size of carton for maximum palletizing density requires considerable effort, computer software is available. Examples are CAPE by CAPE Systems, Inc., Plano, Texas and TOPS by TOPS Engineering Corp., Plano, Texas. An analysis of pallet and trailer loading using CAPE is given in Fig. 21-63*a,b*.

Drums Drums (Fig. 21-42), made of either **steel** or **fiber,** rank next in importance after the multiwall paper bag. For dry solids or slurries, fiber drums predominate; for liquids, the steel drum. Steel drums of the open-head design are used for dry products when the product is hazardous, is to be stored outdoors, or is of a density that will cause reasonable weights to exceed the limits for fiber drums. Although only a few sizes are common, fiber drums can be made to order in almost any size and diameter-length combinations for volumes of 2 to 285 L (0.75 to 75 gal) and for weights ranging from 25 to 250 kg (60 to 550 lb; Table 21-16).

Advantages of the drum are protection of contents, ease of reclosure, and appreciable reuse-resale value. A serious limitation is the inefficient use of space because of the cylindrical shape, which results in high storage and transportation costs. To overcome this, a fiber drum with a square cross section (Ro-Con drum) and the bulk corrugated bag in box have been developed.

Fiber drums decorated with advertising adds $.80 to $3.50 to the basic cost of the drum. The most common type is the multiple-ply kraft-paper body with a steel bottom and a reinforcing top hoop crimpled to the drum. A steel lid, secured by a locking ring tightened by a lever system, fits over the body. For **vapor protection,** barriers are incorporated among the plies, or liners are used as the first ply in contact with the product. Among barrier and liner materials are PE, aluminum and steel foil, polyesters, and silicones. When liquids are to be contained, blow-molded PE liners are used. Free-film PE liners inserted by the user yield a combination of barrier and liner properties at less cost than having the liners as part of the drum body.

Fiber drums are also made with a removable fiber top and a fiber bottom that is either removable or permanently fastened to the body. This drum has limited reuse, but it costs less than the lever-locked metal-top type. Filling equipment consists most commonly of an operator-controlled spout connected to a supply bin resting on a platform scale. Table 21-26 shows the labor productivity of several systems.

Steel drums are made from cold-rolled-steel sheet formed into a cylinder. The longitudinal seam is made by electric resistance welding. The rolling hoops are expanded into the body wall by a special hydraulic fixture, and the ends are crimped to the body to form a leakproof joint. Sealing compounds are often used to assure leakproof joints. The top head has openings to allow installation of the closures or bungs. These closures have U.S. standard-pipe-thread fittings, usually one 2-in and one ¾-in fitting, to allow connection to the loading and unloading equipment.

PACKAGING OPERATIONS

Dry-bulk-packaging operations are divided into two categories: weighing and filling a package that is itself the shipping container and weighing and filling small packages that are in turn placed in outer packages for shipment. The choice of equipment and the way in which it is combined into a system depend on such factors as the product and its chemical, physical, and rheological properties; the type of package to be filled; the total packaging output required; the instantaneous and average rates of filling; cost, attitude, and availability of labor; space available for equipment; storage, shipping, and transportation conditions; cost and availability of capital; seasonality of packaging activity; expected duration of the venture; sanitary, safety, packaging, and working conditions imposed by regulatory bodies; maintainability and reliability of equipment; changes expected in the product and in the demand for it; and nature of the product market (i.e., industrial, consumer, agricultural, or government).

Weighing and Proportioning These are terms used in the packaging industry to describe methods of measuring out an amount of product—into the packaged weight unit which is offered for sale. It could also be done as a process step where a given amount of material must be added to a process on a continuous or a regular basis. With

TABLE 21-26 Performance Data for Packaging Systems

Type of filling and weighing machine	No. of filling spouts	Package detail: Type	Package detail: Size, in	Package detail: Size, mm	Package detail: Construction	Package detail: Closure	Product detail: Material	Product detail: Bulk density lb/ft³	Product detail: Bulk density kg/m³	Product detail: Particle size, U.S. standard§
Fluidizing, SFW‡	4	Pasted valve bag	20 × 25 5 top width	510 × 635 125	4-170 (= 4-ply, 170 lb)	Inner sleeve	PVC‡	38	609	–60 mesh
PWS, open-mouth filler	1	Pinch bag	16 × 5 × 30	405 × 125 × 760	4-170 PE barrier	Adhesive	PE	30	481	⅛-in pellets
Fluidizing, SFW‡	2	Pasted valve bag	20 × 25—5¼ top	510 × 635 135	4-170	Tuck-in sleeve	PVC	36	577	–60 mesh
Fluidizing, SFW	3	Pasted valve bag	21 × 25	535 × 635	4-170	Tuck-in sleeve	PE	30	481	⅛-in pellets
Impeller, SFW	4	Pasted valve bag	18½ × 27½ (face)	470 × 700	3-170	Insert sleeve	Portland cement	94	1506	–325 mesh
Auger, SFW, net-weigh	1	Sewn valve bag	16 × 5 × 28	405 × 125 × 710	4-190	Tuck-in sleeve	PE	32	513	5/32-in cubes
Centrifugal belt, SFW	2	Sewn valve bag	15 × 5 × 36	380 × 125 × 915	3-150 PE barrier	Insert sleeve	Fertilizer	55	881	⅛-in pellets
PWS, open-mouth filler,	1	Pinch bag	17 × 4 × 36	431 × 100 × 915	3-150 PE barrier	Adhesive	Fertilizer	55	881	⅛-in pellets
Fluidizing, SFW	4	Pasted valve bag	18½ × 26 5¼ top	470 × 660 135	3-150 PE barrier	PE inner sleeve	Fertilizer	55	881	⅛-in pellets
PWS, open-mouth, heat sealer	1	PE flat-tube bag	16 × 30½	405 × 775	10-mil PE	Heat-sealed	Fertilizer	55	881	⅛-in pellets
PWS, form-fill-seal	1	F/F/S gusseted bag	16 × 5 × 30	405 × 125 × 760	6 mil PE	Heat-sealed	LDPE	30	480	⅛ in
SFW, liquid fill and weigh	1	Steel drum U.S. DOT 1A1 PG Y	55 gal (208 L)—23.5 in dia. × 34.75 in high	596 × 883	18-ga (0.0428-in) ends, 20-ga (0.0324-in) body	2-in, ¾-in NPT bungs	Lacquer solvent		0.839	sp. gr.
Gravity, SFW	1	Sewn valve bag	16 × 5 × 28	405 × 125 × 710	4-190	Tuck-in sleeve	Polystyrene	32	513	5/32-in cubes
Platform scale, autofill cutoff, SFW	1	Drum	55 gal	208L	6-ply fiber (300 lb)	Lever-locked steel cover	PE master batch	30	481	⅛-in pellets
Platform scale, manual cutoff	1	Drum	55 gal	208L	6-ply fiber (300 lb)	Lever-locked steel cover	Cleaning compound	45	721	–20 to +80 mesh
Platform scale, autofill cutoff, SFW	1	Bulk box, 3-mil PE liner	15 × 15 × 24	380 × 380 × 610	Outer 275-lb test DW‡ liner 600-lb test, DW	Staples	Insecticide, technical grade	40	640	–200 mesh
Platform scale, autofill cutoff, SFW, automatic staple closer	1	Bulk box	41 × 34 × 36	1040 × 860 × 915	Inner, outer boxes: 600-lb test, DW kraft board	Staples	PE	30	481	⅛-in pellets
Vertical auger, SFW	1	Small bag Pouch	10 × 4 × 25 14 × 27	255 × 100 × 635 355 × 685	3-120 paper, 2- to 4-mil PE	Glued, heat-sealed	Insecticide powder	20	320	–325 mesh
Vertical auger, SFW	1	Folding box	6½ × 3½ × 9	165 × 90 × 230	12-point reprocessed board with 2-mil PE liner	Glued, tied PE liner	Sprayable insecticide powder	20	320	–10 μm
Form-fill pouch maker, PWS	2	Pouch	8½ × 15	215 × 380	1- to 3-mil PE film	Heat-seal, hot-wire cutoff	Detergent, spray-dried	39	625	–30 to +60 mesh
Baler, manual package in feed, mechanized closing	—	Baler bag	23 × 30	585 × 760	2-140	Glued	12, 5-lb (2.3 kg) bags herbicide	45	721	–325 mesh
Corrugated case, manual package in feed, mechanized closing	—	Regular slotted carton	24 × 16 × 7	610 × 405 × 180	275 DW	Glued	12, 5-lb (2.3 kg) bags herbicide	45	721	–325 mesh
Carousel liquid filler	18	Round jug	4.8d × 9.7h	96d × 223h	Plastic 100 gr.	38 mm cap plastic	Laundry bleach	—	—	1.1 sp. gr
In line liquid filler	6	'Boston Round' bottle	3.8d × 8.7h	123 × 245	Glass	33 mm cap plastic	Isopropyl alcohol USP	—	—	0.9 sp. gr

*Fractions indicate the portion of a person's time required to perform activity; these are additive to compute the number of people needed.

†Includes equipment and installation but not building or services needed.

‡Definition of abbreviations: SFW = simultaneous fill-and-weigh; PWS = preweigh scale; SMC = sewing-machine closer; DW = double wall; SOM = sewn open-mouth; PE = polyethylene; PVC = polyvinyl chloride.

§Metric equivalent of particle sizes given elsewhere.

[1]For existing equipment, remanufactured to new machine standards and guarantees, multiply the above investment values by 0.5.

[2]Where [2] is shown after the system investment, add $181,000 for an automated inspection system comprising an X-ray metal detection machine, and 3 machine vision units to verify closure in place and label and bar code are correct and in place.

[3]Investment data courtesy of In Plant Packaging Systems, Inc., Metuchen, NJ.

[4]The above data is useful in comparing alternative systems and for order of magnitude investment values. However, for capital and other budgets, recent actual quotations from manufacturers should always be used.

Weight of contents		Packaging rate, packages/min		Weight variation from average		Packaging personnel needed*				Package handling		Approximate 1996 investment ($ × 1000)	
lb	kg	Avg	Instant	oz	gr	Package setup, supply	Filling-machine operators	Package closers	Palletizers, loaders, attendants	Package conveyorized	Automatic palletizing	Filling machine[1]	System[2]
50	22.7	12	17	4	114	1	1	0	2	Yes	No	110	437
50	22.7	8	12	0.5	14	1	1	1	2	Yes	No	45	200[3]
50	22.7	6	8	4	114	1	1	0	1	Yes	No	78	330[3]
50	22.7	16	24	3	85	1	1	0	1	Yes	Yes	96	550[3]
94	42.7	22	28	8	227	1.5	1	0	0.5	Yes	Yes	110	655
50	22.7	1	2	3	85	0.25	0.25	0	0.5	No	No	27	52
80	36.4	12	16	8	227	1	1	0	2	Yes	No	66	330
80	36.4	16	22	4	114	1	1	2	2	Yes	No	44	240
80	36.4	18	24	16	455	1	1	0	2	Yes	No	119	350
50	22.7	18	24	4	114	1	1	1	2	Yes	No	66	285
50	25	8	12	1	28	1	0	0	0	Yes	Yes	1,075	3,300[3]
385	175	2	3	6	170	0.25	0.5	0.5	1.75	Yes	No	116	178
50	22.7	0.2	0.4	16	455	0.25	0.5	0	0.25	No	No	7	13
250	113.6	1	4	2	57	1	0.5	0.5	1	Yes	No	27	110
300	136.4	0.5	1	0.5	14	0.25	0.25	0.25	0.25	Yes	No	7	28
100	45.5	0.5	1	4	114	1	1	1	1	No	No	45	87
900	409.1	0.33	0.50	8	227	2	0.75	0.25	—	Yes		45	218
10	4.5	5	10	1	28	1	1	1	3	Yes	No	21	110
1.5	0.682	8	12	0.5	14	1	1	1	3	Yes	No	21	45
2.5	1.136	10	12	0.5	14	1	—	—	2	Yes	No	110	153
60	27.3	1.5	3	—	—	0.5	0.5	0.5	0.5	Yes	No	45	66
60	27.3	1	2	—	—	0.5	0.5	0	1	Yes	No	30	45
64 fl.oz.	1.81	40	50	±0.1 fl.oz.	3cc	0.5	0.5	0.5	0.5	Yes	Yes	175	750
32 fl.oz.	0.941	14	18	±0.1 fl.oz.	3cc	0.5	0.5	0.5	0.5	Yes	No	55	256

each, certain degrees of precision are required. There are several terms which are used by the scale industry. A **net weigher** (Fig. 21-43) is a device with a scale system for weighing bulk solid materials. The analog of the weight being measured is sensed by a mechanical or an electrical sensor system. Sensor output is interpreted by a control system, either electrically or mechanically or by a combination of both, which controls the flow of product into the scale and hence the weight. Net weighers are rarely used for liquids. The term **gross weigher** applies to a type of device which is becoming obsolete in the packaging industry. This type of device has a relatively large equipment mass holding the package into which the product is being weighed, with the result that high weight accuracy is not possible. The term **proportioning** is used to describe a system where a given volume of material is moved in a given period of time into a weigh vessel—often the package itself—without the weight actually being sensed. Proportioners operate under the assumption that product density is constant. For liquids, this is usually true at any given temperature. For solids this is rarely true. As a result, proportioning devices rely heavily on either having constant density or relatively uniform density which varies only slightly over time. An example of a volumetric filler is given in Fig. 21-44. This device is a vertical auger designed for filling powdered materials into glass jars. The assumption of constant density is applied. The machine is set for the required time to fill the desired weight into the package. This type of device has benefited from the microprocessor era in that downstream check weighers are used to determine the net weight packaged in each container. Using a software to calculate trends, the check weigher sends a signal to the proportioning device to increase or decrease the filling time because the weight being filled now shows a trend to drift as a result of density change. As the density increases, for the same constant period of time the filled weight will increase. The converse is true when the density decreases.

There are two principal types of package-weighing and -filling equipment: **simultaneous fill-and-weigh,** with which the material is weighed as it is poured into the container; and **preweigh,** with which the material is weighed prior to being poured into the package. The former applies mainly to valve bags, pouches, bulk boxes, and bags in boxes; the latter, to open-mouth bags, small bags, and cartons, to form-fill-seal, and, at times, to valve bags.

There is a further distinction between net weighers and gross weighers. **Net weighers** are defined by the ratio (0.3 to 0.5) of weight of charged material to weight of weighing vessel and associated parts. Preweigh scales are examples of net weighers. With **gross weighers,** of which simultaneous fill-and-weigh is an example, the ratio is usually greater than unity. Net weighers are accurate within ±0.125 to ±0.25 percent; gross weighers, from ±0.5 to 1.0 percent. Maintaining certain scale-feed conditions is critical in obtaining accuracy and sustaining a given production rate; appropriate feeding devices and surge bins are of great importance. If desired, weight accuracy can be increased, at greater cost, by special modifications and accessories such as load cells and microprocessor controls, bulk and dribble devices, and feeders and bulk density tracking software.

The **weight accuracy** of a dynamic weighing device is expressed as a plus or minus percentage deviation from a given *set weight,* which can only approximate the desired *actual weight.* The dynamic nature of weighing requires that the scale respond to changing static conditions as well as to a series of constant dynamic conditions. Minor variations in product density can cause the set weight to drift, the result being unacceptable packaged weight. Scale sensitivity is often suspected to be at fault, when in fact it is the set weight that has drifted. This is easily verified by check-weighing a series of weighings and determining their standard deviation.

Check Weighing Because of drifting set weight and the influence of federal and state legislation on allowable deviation from

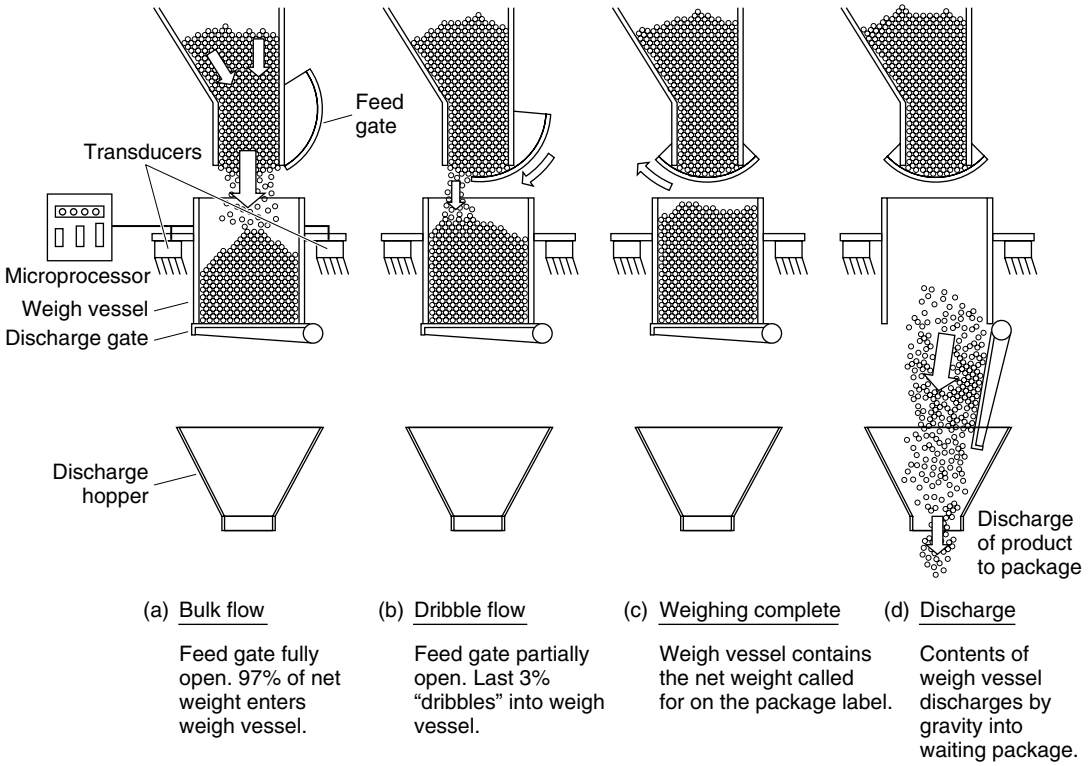


FIG. 21-43 Netweigh scale operating concept.

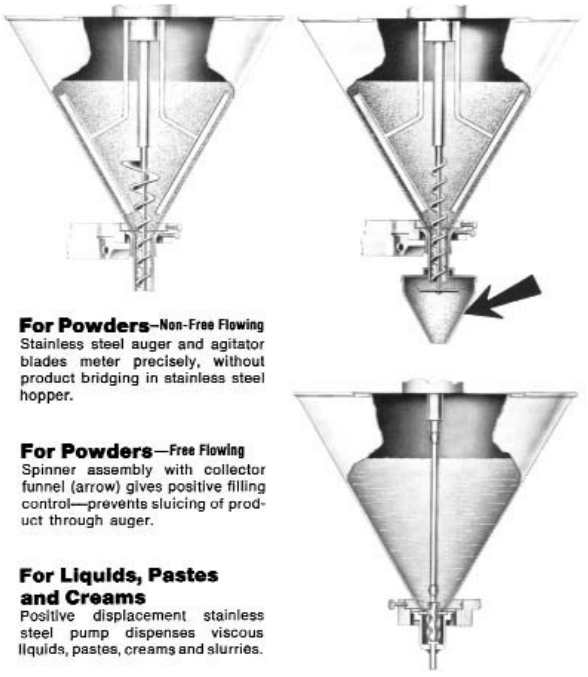


FIG. 21-44 Volumetric proportioner designs for various product types and consistencies. (*Courtesy of Mateer-Burt Co., Inc., Wayne, PA 19087.*)

advertised weights, a major new phase of package filling and weighing is that of check weighing. This can be done manually with a platform scale and then following a simple statistical procedure and control chart. There are devices applicable to preweigh scales which perform and record a static weighing just prior to discharging to the filling machine. There are in-line check weighers that weigh each package and pass or reject it depending on its weight, and keep a log of the results. One development permits continuous automatic readjustment of the scale set weight by means of a microprocessor that records each weighing and then, from a series of these, computes whether or not the set weight is drifting. An automatic adjustment is then made. The use of high-accuracy transducers aids this process.

Filling and Weighing Equipment Of special interest in the selection of filling equipment from the wide variety available (Table 21-26) and combining it into the total system is the equipment's relation to instantaneous output, average output, and personnel. Methodizing, subdividing into work elements, and prediction of the time required for each job function by means of standardized data such as methods-time measurement (MTM) and general-purpose data (GPD) permit accurate identification of jobs and work content. Actual average output can thus be calculated and, from this, the instantaneous output.

Instantaneous rate, which is the rate that equipment manufactuers imply in their guarantees of performance, is defined as the number of packages produced per minute with the equipment operating under steady-state conditions. **Average rate,** the measure that the user needs to plan production and output commitments, can be defined as the arithmetic average (packages per minute) produced over a production shift (usually 8 h). Equipment reliability must be taken into consideration in determining average rates because malfunction downtime can have a significant effect on rate values. Also, the effect of production scheduling on equipment idle time and changeover from one product to another needs to be considered.

Valve-Bag-Filling Equipment Although multiwall paper bags and plastic bags can be filled by a wide variety of equipment, the simultaneous fill-and-weigh (gross-weigher) type predominates. Net-weigher-type equipment using a preweigh scale which discharges into a valve-bag filler is finding increased favor when greater weight accuracy is required. The most widely used category is the gross weigher of the pressure-fluidizing type, for which these parameters and ranges hold:

Parameter	Capability range*
Particle size	⅜-in (9.5-mm) pellets to submicrometer
Bulk density	0.5 to 200 lb/ft^3 (8 to 3200 kg/m^3)
Filling spout	1 to 4
Bagged weight	20 to 150 lb (10 to 70 kg)
Bagged volume	1 to 6 ft^3 (0.03 to 0.17 m^3)
Material of construction in contact with product	Carbon steel, stainless steel, plastic-coated steel, aluminum
Output capability	1 to 30 bags per minute
Bag-valve size	3 to 5½ in (75 to 140 mm)
Weight error: simultaneous fill-and-weigh scale	+2 to ±4 oz (60 to 120 g)
Weight error: preweigh scale	±1 oz (30 g)

*SI equivalents are rounded off.

Fluidizing Bag Fillers These fillers can meet any production requirements, ranging from pilot-plant scale through heavy-duty, conveyorized high-tonnage installations. A chamber is provided with an air pad at the bottom, adjacent to a filling spout. A column of product over this section, which is what causes flow, may be opened to the atmosphere or enclosed and pressurized. When the desired bag weight is reached, a system is activated by the integral weigh scale to close the valve through which material flows to the bag. Fluidizing and pressurizing air is best provided by a positive-displacement blower at 1.5 kW (3 hp) per filling spout.

Of special interest on multiple-spout conveyor-equipped fluidizers and on certain types of screw and belt filling machines is a combination operator's seat, bag rest, and tuck-in-sleeve work aid. This device places the operator in an optimum work position after filling, to allow easy and positive tucking of the sleeve. Extensive use of the polyethylene film internal sleeve, however, has reduced the significance of the tuck-in-sleeve feature. Several types of heat-sealable valve-bag sleeves are available, as is equipment for closing them automatically. These are used when even slight leakage of product from an internal sleeve bag is unacceptable.

Bags can be automatically placed on valve-bag packers by means of an **automatic bag-placing device,** which consists of a magazine holding approximately 100 empty pasted valve bags and of a mechanism for removing the bag from the magazine, opening the valve and placing it on the filling spout, and initiating the filling-discharge cycle. The device's installed cost can be recovered in about 1 year's operation, based on typical wage rates paid in the United States for packaging-line labor.

Auger or Screw-Type Bag Fillers These fillers are usually applied to tuck-in-sleeve-type valve bags, for which production rates of one to two bags per minute and weight error limits of ±1 percent are required. Single-screw filling-spout designs (ordinarily of the net-weigh type) with simultaneous fill-and-weigh features are most common.

Gross-weight fillers need a feeding device such as a screw, vibrator, or belt, depending on the product. Particle size from 12.7-mm (½-in) pellets to 44-micrometer (325-mesh) powders can be handled, as can bulk densities ranging from 80 to 3200 kg/m^3 (5 to 200 lb/ft^3). Power requirements range from 373 W to 5.6 kW (0.5 to 7.5 hp). Weight accuracy is obtained by braking the motor to a rapid stop once the correct weight has been reached and the scale system has actuated the electrical or mechanical control system. Although fluidizing packers have diminished the importance of the screw type, the latter will always find application when space is a problem and investment must be low.

Centrifugal Belt-Type Packers This packer is used to a limited extent for granular or pelleted products whose bulk densities range from 400 to 1600 kg/m^3 (25 to 100 lb/ft^3). Single-spout, simultaneous fill-and-weigh fillers, which consist basically of a short-belt conveyor, handle one to three bags per minute at weight accuracies within ±1 percent; the two-spout design is most common in high-speed con-

veyor-equipped installations, with which preweigh scales are used. Up to 30 bags per minute can be handled, with weight accuracy within ±0.1 percent or better.

Impeller-Type Fillers Used extensively for finely divided materials such as portland cement, plaster, lime, and talc, these fillers contain an impeller that turns in a casing (similar to a centrifugal pump) to move the product into the bag. Most impeller machines are installed with conveyors, although single-spout machines have been used when bag handling is done manually. Bulk densities are limited to 800 kg/m^3 (50 lb/ft^3) and higher. Portland-cement filling rates of up to thirty 43-kg (94-lb) bags per minute are possible with weight accuracies within about ±2 percent. Power requirements range from 3.7 to 7.4 kW (5 to 10 hp) per filling spout. Impeller fillers are being superseded by the fluidizing type because of the latter's better weight accuracy, cleanliness, and reduced investment and operating cost.

Gravity-Type Fillers These fillers are available in either the gross-weigher type or the net-weight type using a preweigh scale. Gross-weigher types are used in marginal operations for which investment must be limited and performance is not critical. Packing rates of 0.5 bag per minute and weight accuracies within ±5 percent are possible. Only free-flowing pellets and granules can be handled practically. The net-weight type utilizes a highly accurate preweigh scale which is placed 3 to 5 m (10 to 15 ft) over the bag-filling spout. Gravitational energy of the falling charge of product is used to force the product into the bag. Rates of up to six 25-kg (50-lb) bags per minute per scale-fill spout unit are possible. This type of equipment requires a free-flowing material and can handle the range of 250-micrometer through 4.8-mm (60-mesh through 4-mesh) pellets. Bulk densities as low as 400 kg/m^3 (25 lb/ft^3) can be handled.

Open-Mouth-Bag-Filling Equipment Two considerations in choosing this type of equipment (Table 21-26) and in deciding between open-mouth and valve-bag systems are the labor required for a given output and the capacity limitation of the closing system. With open-mouth bags, weighing and filling are usually done by a net-weight preweigh scale; gross weighers are sometimes used on low outputs. Operating principles and installation practice for automatic scales have been described earlier in this subsection.

Preweigh scales discharge to a chute system to which a bag is attached. The kinetic energy of the charge as it reaches the bottom permits the bag to stand without lateral support on a closing-machine conveyor. The filled bag is then dropped to a short-belt conveyor that passes the bag through a closing machine. Empty bags are held onto the chute system by hand or by a bag-clamp arrangement. These scales handle from 8 to 35 charges per minute. Weight accuracies are commensurate with product value and weight laws.

Bag Closures Conventional multiwall paper open-mouth bags are closed by sewing; the pinch-bottom type, by hot-melt adhesive. Three styles of sewn closure are used. The simplest and fastest consists of sewing with cotton or polyester thread, with needle and looper threads entwined in a chain-fashion stitch. This is adequate for low-cost products, for which sifting through the sewing is not objectionable. An improved method consists of adding a flat tape over the open mouth and sewing through it with the needle and looper threads. An additional thread, called filter cord, can be added between the needle thread and the tape to increase siftproofness, but this reduces closing rates.

Complete **siftproofness** can be had by the "tape-over-sewn" procedure, whereby the tape is glued onto the finished sewn closure by a device downstream from the sewing head. For siftproofness at high production rates, the pinch-style glued closure is used. The pinch-bag closure has the adhesive preapplied to the open end by the bagmaker. After the bag has been filled, the closing machine reactivates the adhesive by heat prior to sealing.

Polyethylene film bags are closed by heat-sealing together the face and back of the bag. The closing unit consists of a pair of belts that support the top of the bag and guide it through a heated section that fuses the face and back. This is followed by a cooling section.

Drum and Bulk-Box Filling This process consists of three operations: setting up, filling and weighing, and closing. Because setting up bulk boxes is cumbersome, a well-methodized workplace, equipped with work aids, is recommended. Weighing and filling can be done manually or automatically. There is enough similarity between the two ways for manual systems to be mechanized later.

The most common installation consists of a conveyor line with a platform scale at a central location. This scale may be a simple dial type, which the operator watches to stop flow. The first mechanization step is to add a cutoff switch to the scale. Filling rates of 5 to 10 kg/s (10 to 20 lb/s), with weight accuracies within ±1 percent, are possible. Check weighing is easily accomplished by observing the net weight on the dial. A skilled worker can operate a manual system to within a few grams or ounces of the desired weight. Preweigh scales are occasionally used for free-flowing products, when the net weight is 100 kg (200 lb) or less or is a multiple of a weight that can be set on the scale and repeated to get the desired total weight. The main advantage of preweighing is higher accuracy.

Maintenance This is an important consideration in the operation of a packaging line. It is especially true with the advent of microprocessor control and the sophisticated devices for sensing of packaging-process variables. Two requirements for successful maintenance are needed. First is skilled technicians capable of handling the electronics as well as the mechanical parts of the packaging line. The community colleges are a source of skilled maintenance technicians. The second is the availability of repair parts. In the present industrial environment these are usually minimized and confined to those which are known to fail or which are prone to premature wear. Such parts are usually maintained in inventory. However, other parts are usually available on an overnight basis from equipment suppliers regardless of location. This is true whether the equipment is made outside the United States or the country of use. The overnight-shipping services such as Federal Express make minimum stocking a practical reality. With the use of microprocessors the trend is to have duplicates of all of the circuit boards in the plant inventory. Should there be a failure, the board can be replaced immediately and the old board returned to the maker for remanufacturing.

Small Packages These are of importance in the consumer chemical and the reagent chemical businesses and for shipping samples of products. Bulk solids, liquids, and gel-type products are involved. For bulk solids such as powders, granules, and pellets, the most often used packages are folding cartons, multiwall paper pockets (bags), or form-fill-seal plastic bags. For liquids, glass or plastic bottles and jars are used. Weight units are typical up to 20 lbs, or 10 kg. Volume units are typical up to 1 gallon or 4 liters. Where the product is a gel or a thixotrope, jars are used, with weight unit to 1 lb, or 0.5 kg.

Low-speed operations for these packages use in-line-type equipment in which transfer in, filling, and transfer out are sequential. Rates of production are typically 10 to 20 packages per minute. For high-speed packaging, the in-line equipment is usually too slow or requires a high investment for multiple lines. High-speed filling is typically 40 to 100 packages per minute, but it is not unusual to find certain products packaged at over 100 units per minute. To obtain such production rates, the packaging machinery industry has developed a carousel type of equipment wherein the filling operation is continuous. The package enters at one end of the carousel, is filled as it moves around the carousel, and is discharged having the required weight or volume of product. From that point it moves to a capping or closing machine. Figure 21-45 shows a carousel unit for liquids in bottles or jars. An example of an in-line liquid filler is shown in Fig. 21-46. Figure 21-47*a* shows a carousel-filling unit for bulk solids. Small-package operations for bulk solids involve two main procedures: filling and closing.

Weighing and filling may involve either preweighing scales, proportioners, or simultaneous fill-and-weigh. Preweigh scales are preferred when high weight accuracy is required. With appropriate package-handling equipment, these weighing devices can be used to fill cartons, bags, jars, or bottles. Preweigh scales of the multiple or "gang" arrangement are used to obtain both high accuracy and rates of production on dry products. One design uses 17 separate preweigh scales. Each weighs a charge equal to one quarter of the desired weight. A process-control computer monitors all weigh vessels and selects the four whose sum of weights is nearest to the desired weight and directs the weigh vessels to discharge to the waiting package. Accuracies of 1 gram in 1 kg are typical, and production rates of 150 weighings per

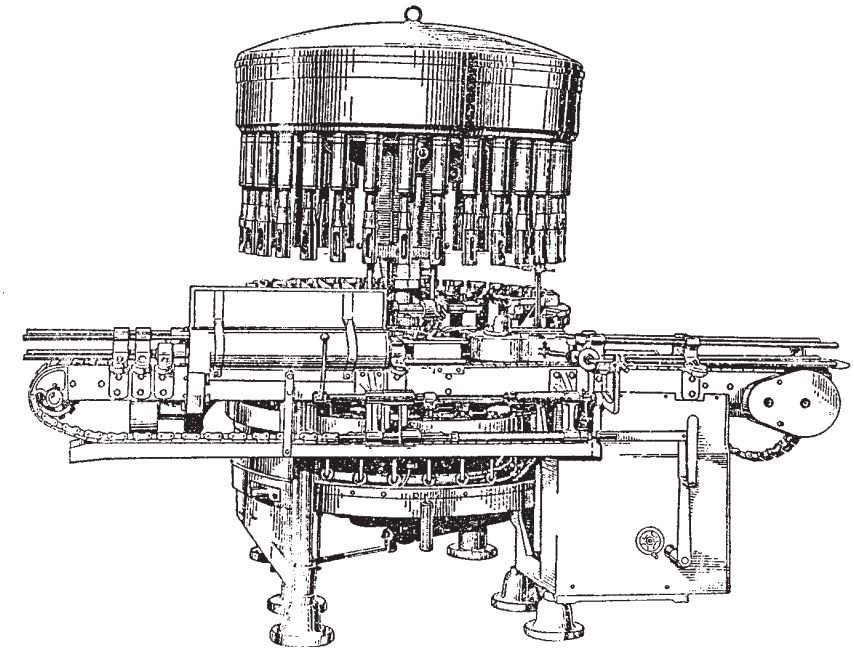


FIG. 21-45 HORIX 32 station carousel-type liquid filler for glass and plastic bottles and metal cans.

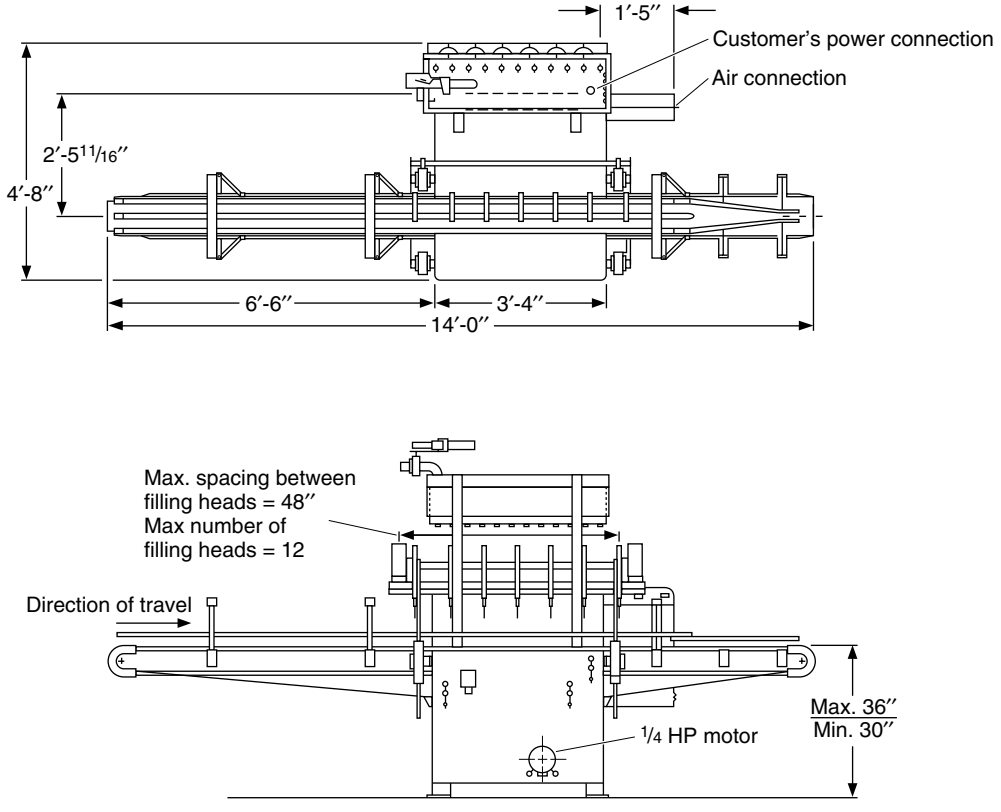


FIG. 21-46 In-line, 6-head, 2-lane filler for liquids in glass and plastic bottles and jars. (*Courtesy of National Controls, Inc., Baltimore, MD.*)

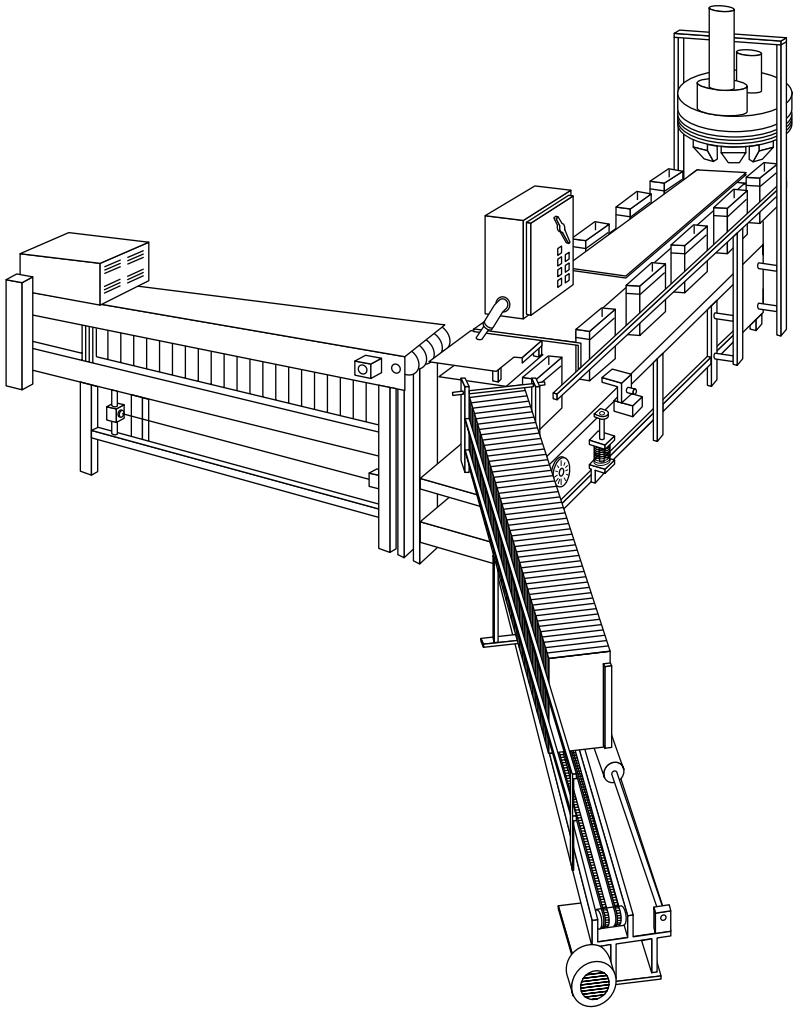


FIG. 21-47*a* Clybourn carousel-type folding carton set-filler-closer for bulk solids such as powders and granules. (*Courtesy of Clybourn Machine Co., A Division of PAXALL, Inc., Skokie, IL 60076.*)

minute are possible. Figure 21-47*b* illustrates a "gang"-type scale system. Figure 21-47*c* shows how such a weighing system can be integrated into a business record-keeping system.

Where folding cartons are to contain a product which is sensitive to moisture pickup, barriers are available which can be incorporated into the carton construction. An example of this is polyethylene laminated to paperboard. In some cases an insert bag is used instead, but this requires an additional operation and is usually accomplished by a form-fill-seal machine that makes a bag which is then inserted by another machine into the folding carton.

Form-Fill-Seal Premade small packages, when filled at high rates, present a problem because of the need to handle and store empty packages. To cope with this requirement the form-fill-seal type of packaging, which not only simplifies the supply problem but produces a superior package, has evolved. This method involves two main functions: a weigh cycle and a package make-fill cycle. Rates of up to 50 packages per minute are possible, with multiples of this rate on machines with two or more stations. Preweigh scales are of the same type used for small-package filling. Figure 21-47*d* illustrates the principles of a form-fill-seal (F/F/S) machine.

At present, form-fill-seal is limited to products having reasonably free-flowing particles with low dust concentrations. Because heat sealing to form the pouch has been largely responsible for the success of this system, thermoplastic films or other plastics and papers with a thermoplastic coating are required. The choice of form-fill-seal versus premade packages depends on economics but usually applies to materials that are nonseasonal.

Large-size form-fill-seal equipment for industrial packages has been introduced. Capable of packaging 25-kg (50-lb) bags, such units use PE sheeting or tubing in roll form. A bag is made just prior to being filled. An advantage of this system is lower labor and material costs, but this is offset by the increased complexity of the equipment. Rates of eight to twenty 25-kg (50-lb) bags are possible. Since preweigh scales are used, high accuracy can be attained.

Carton and Baler-Bag Loading, Wrapping, and Sealing Corrugated boxes may be used for shipping flexible or rigid small containers; baler bags, for flexible ones. Corrugated boxes are loaded manually, semiautomatically (manual loading of the carton set up by machine), or fully automatically. Manual setup and loading are practical for up to 3 cases per minute, semiautomatic up to 10, and automatic up to 40. Associated with each are conveyors that bring packages to the carton loader and remove filled cartons from the sealer.

Carton sealing is carried out automatically by adhesives, tape, or staples or manually by tape or staples. Carton closer-sealers have

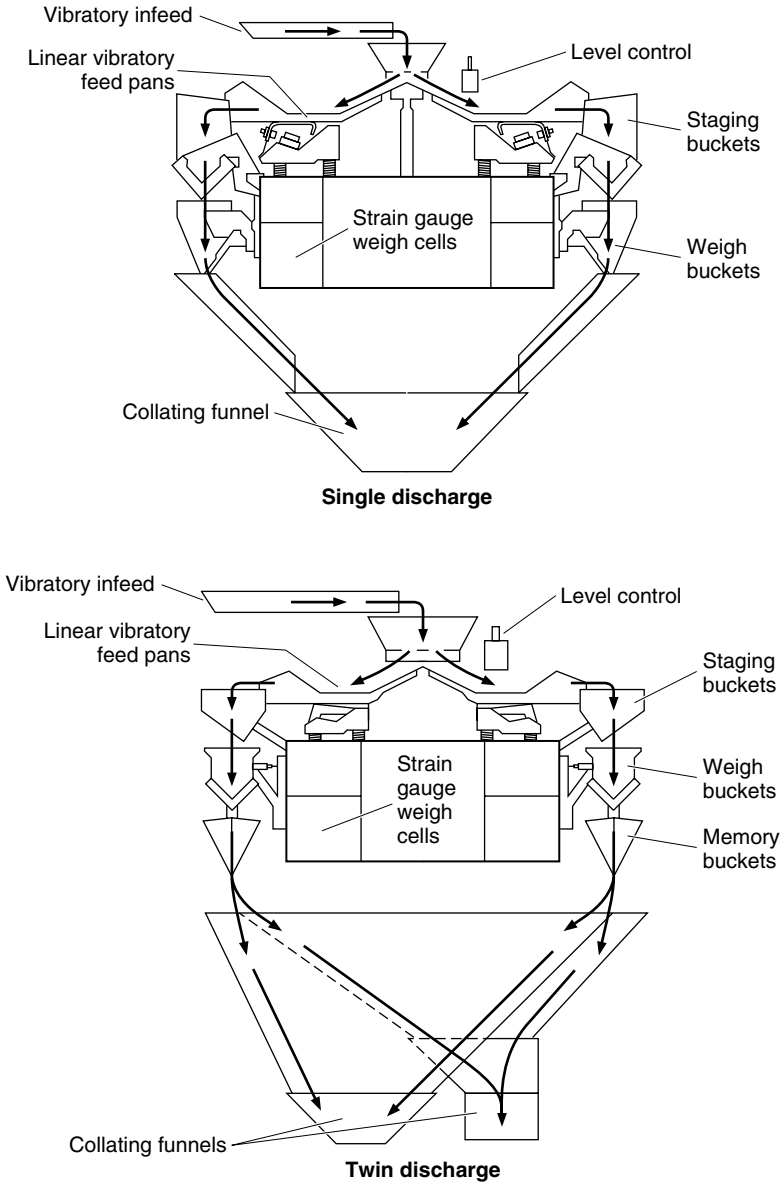


FIG. 21-47*b* Hayssen Yamato "Dataweigh" gang-type scale system. (*Courtesy of Hayssen Mfg. Co., Duncan, SC 29334.*)

become so attractively priced that small operations can justify their use even when the balance of the line is manually operated. Case closer-sealers that take different package sizes in random order are available.

Baler bags can be manually loaded, but the preferred practice involves specifically designed compression units. Their use permits making an integral load in which all package parts share the forces imposed by shipping. A manually loaded compression unit handles 2 to 4 balers per minute; semiautomatic units, with a mechanical package feed and a manual baler-bag application unit, can handle 15 to 20. Baler bags are automatically closed with tape or adhesive, the latter being preferred especially for automated operations.

Wrapping, Bundling, and Shrink Packaging These techniques have limited applications for chemical products. Wrapping and bundling are substitutes for cartons and baler bags, their advantage being that the package is made from roll stock.

Shrink packaging is a significant development. The most important application in the chemical industry is in unitizing packages for palletized shipment. A cover of shrinkable PE film serves to bind a pallet load and permit it to absorb considerably higher transportation forces than it would if packed by any other method. Palletizing, adhesives, and strapping are eliminated, which offsets the cost of the shrink wrap. But it is the reduced damage in shipment that makes shrink wrap so economically attractive.

The hand-applied shroud of shrinkable PE usually consists of a premade bag large enough to envelop the load. Equipment to shrink the wrap ranges from small propane-fired hand-held units, which take

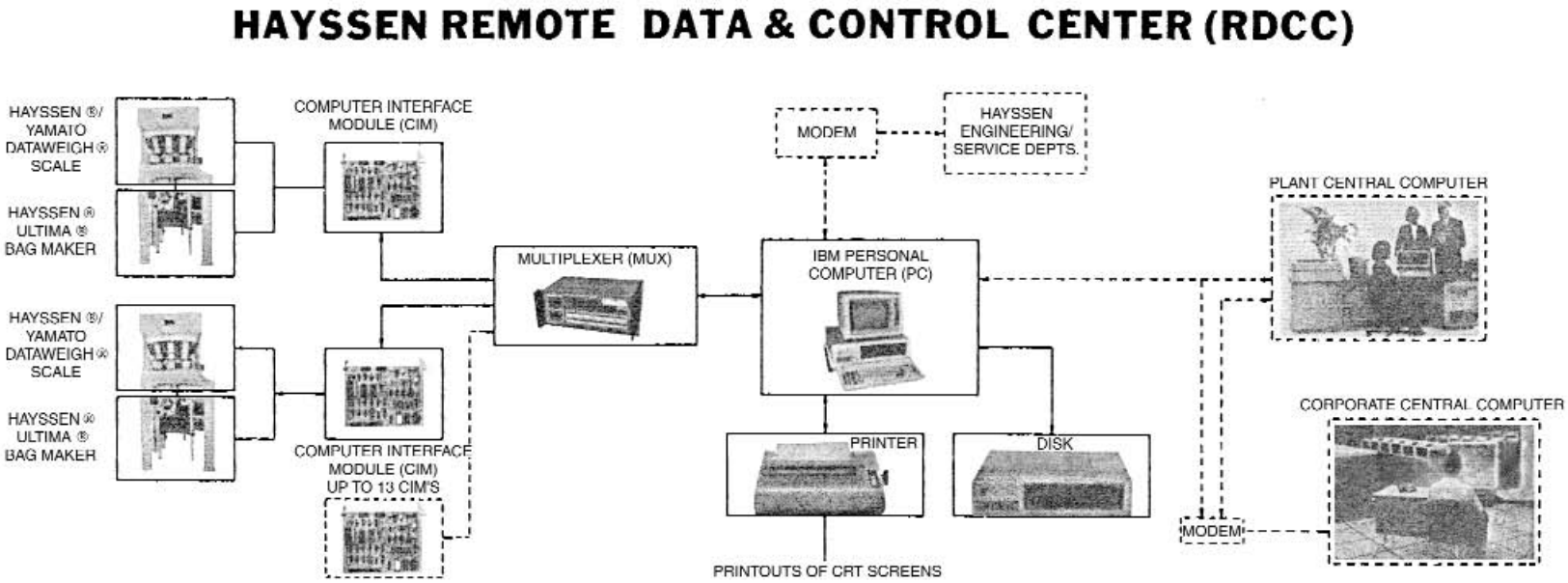


FIG. 21-47c Business data and report system using output of Hayssen Yamato "Dataweigh" scale as input to computers. (*Courtesy of Hayssen Mfg. Co., Duncan, SC 29334.*)

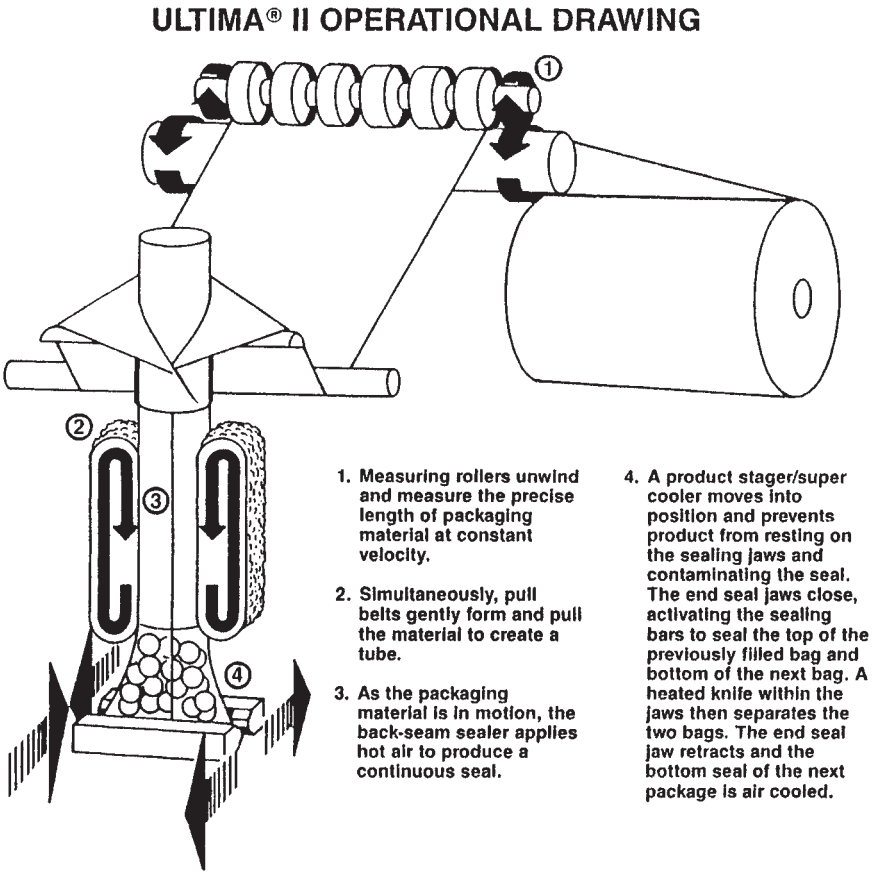


FIG. 21-47*d* Hayssen patent no. 4,288,965 form/fill/seal bag-making system. (*Courtesy of Hayssen Mfg. Co., Duncan, SC 29334, 864-486-4000.*)

about 5 min to shrink a 1-ton load, to fully automatic conveyor lines handling up to 30 pallets per minute.

Stretch-Wrap Packaging This type of packaging is an alternative to shrink packaging. It consists of wrapping a pallet load of product with a thermoplastic film which is applied under tension and which envelops the sides of the entire load. Special machinery accomplishes this procedure correctly. An advantage of stretch wrap is that it does not require the precise fit and shrinkage properties of a shrink-wrap bag to ensure tight binding of the load to the pallet. As long as the stretch film meets tensile and elongation properties and the stretch-wrap machine is in proper adjustment, a satisfactory result will be obtained. Material cost for stretch wrap is 75 to 100 percent of that of shrink wrap. An economic advantage is that stretch wrap is less energy-intensive than shrink wrap by a factor of 100 or more. Labor requirements are also less, in that one operator can start the stretch-wrap process by attaching the film to the pallet and the machine completes the operation automatically. With shrink-wrap, two operators are usually needed because of the unwieldiness of the shrink bag.

Batch Inclusion Packaging This has been the result of the environmental consciousness of the chemical industry worldwide. The meaning of this term is that the product contained in the package and the package itself are added to a process and the packaging material actually becomes part of the product being made. By way of example, an antioxidant in a batch inclusion package is added to a polyolefin compounding operation. Not only is the antioxidant incorporated into the product but so is the package. The package material is chosen such that it is compatible with the end product and usually represents a minute fraction of that end product. A second advantage is that many companies offering this type package will offer a specific weight requested by the customer, which simplifies their formulating operations. The development of strain gauge-microprocessor-controlled weighing equipment allows packagers to offer custom package weights at little additional costs over offering a single size. A marketing advantage can come from this type of customer service. A wide variety of film-type materials are available to packagers. These include polyethylene, polypropylene, nylon, polycarbonate, partially polymerized rubber, fluoro-chloro-ethylene polymers and others. Predictions have been made that in a matter of a few years most industrial chemicals will be packaged in batch inclusion packages. The reason is there is no costly disposal of empty packages which, depending on the contained material, may be subject to government disposal regulations.

Fine-Particle Packaging This term is applied to powders and similar finely divided materials. These present significant flow problems in material handling and packaging. Surface chemistry, particle shape, and electrostatic forces have a great effect on flowability. Weighing and filling of fine powders in plastic packages is a difficult and sometimes impossible task because of these characteristics. While much work has been done in the characterization of fine particles the development of packaging machinery to handle such difficult products remains more art than science and engineering. A notable effort in packaging such materials is that by William J. Runo of Allentown, Pennsylvania, who has developed a process which uses compressive shock to orient particles and drive them into the package so that they occupy minimum volume and consequently have maximum possible density. This process is proprietary and is licensed by Dr. Runo. An example of the ability to increase bulk density is a product having an

average particle size of eight microns and a loose bulk density of 8 pounds per cubic foot (0.128 grams per cc) which was increased to 24 pounds per cubic foot (0.385 grams per cc). The principle of operation of the Runo system is that it is independent of the package type and can be used on all types of packages used for chemical products—drums, bags, batch inclusion bags, bulk bags, and others—by having the appropriate holder for the package.

Chopped-Fiber Packaging This type of packaging is complicated by a geometry of the fiber. The ratio of fiber length to diameter can be several thousand with the result that it is impossible to obtain any degree of uniform flow of the fiber into packaging machinery, into the package itself, or when the fiber is being handled, as during incorporation into a product such as a composite. A proprietary process for accomplishing uniform feeding of chopped or milled fibers is described by U.S. Patents numbers 4,669,887 and 4,953,135. This technology can be licensed and apparatus purchased from Lee Technologies, Inc., Huntington, West Virginia.

Labeling This has become a very complex issue. Labeling requirements for the products of the chemical industry are regulated by the U.S. Department of Transportation, the Occupational Safety and Health Agency, the Environmental Protection Agency, and other government organizations. Customers may also require special labeling. Requirements mandated by government must be strictly adhered to. In many states, the right-to-know laws impose additional requirements. Products of the pharmaceutical industry have additional requirements imposed by the Food and Drug Administration (FDA).

While the foregoing refers principally to the information the label must contain, there is the further consideration of how the label is to be printed, the inks which are to be used, the method of adhering the label to the package, and the method of applying the label. Application methods can range from hand to automatic machinery applications. Influencing label production and strongly benefiting it is the advent of the personal computer. Labeling systems are available in which the information is entered through a terminal, it is displayed on a CRT, and when complete, the microprocessor directs a laser type or a dot matrix printer which prints the complete label which must be attached to the package. Figure 21-48 illustrates such a label. Another system actually sprays information onto the package as it passes by the labeler which is adjacent to the package conveyor. Figure 21-49 illustrates this type of noncontact system.

Label information may be divided into two classes, that fixed for each container and that which varies from package to package or from batch to batch. Examples of fixed information are name and address, net weight, name of product, and warnings about product hazards. Variable information includes batch, blend, or lot number, consecutive package number, coded information, and possibly date of manufacture. Export packages require outside-package dimensions and the gross, tare, and net weights in U.S. customary and SI units. When there is uncertainty as to label requirements, experienced legal advice should be sought. Fixed information is usually printed by the package maker. Variable information can be applied manually with rubber stamps or stencils or by automatic in-line marking equipment.

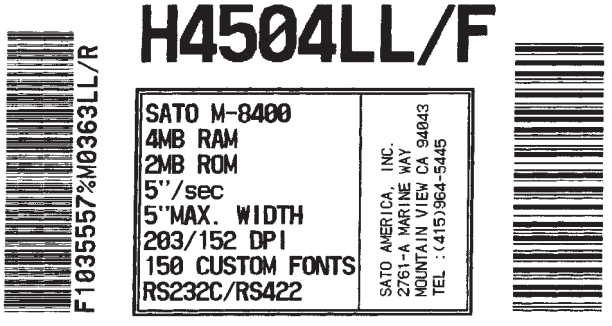


FIG. 21-48 Label example printed by a high density dot matrix printer. (*Courtesy of SATO AMERICA, Inc., 2761-A Marine Way, Mountain View, CA 94043.*)

Bar Coding Bar coding represents a major advance in being able to track identities and inventories of products on a real-time basis. The impetus for the development of bar coding was the Universal Product Code (UPC) developed under the auspices of the American grocery industry for the purpose of allowing automatic reading of product and price information at the checkout counters of supermarkets and mass merchandisers. It has since grown into a widely used system to track an inventory item or group of items. It has facilitated the use of automatic storage and retrieval systems (ASRS) described later in this section. There are currently five types of bar codes in use worldwide, illustrated in Fig. 21-50, (*a*)–(*e*).

Universal Product Code (UPC) See Fig. 21-50(*a*).

- Incorporates numeric characters only.
- Usually includes 12 digits and allows bidirectional scanning.
- Zero-suppressed version is printed using seven digits.
- Check digit is incorporated into code.
- Quiet zone is nine times the narrow bar width on both the left and the right.
- At 100 percent magnification, required size for a 12-digit UPC with the quiet zone is approximately 1.5″ horizontally and 1.0″ vertically.
- EAN variations are used in Europe.
- Common applications include retail, packaging, counting, and data processing.

When scanned, the UPC will be decoded as a 12-digit number. These 12 digits represent the following: digit 1 is the number system character; digits 2, 3, 4, 5, and 6 make up the manufacturer's ID number; digits 7, 8, 9, 10, and 11 are the vendor's item number(s); digit 12 is the check digit.

When scanned, the UPC zero-suppressed will be decoded as a 12-digit number. These 12 digits represent the following: digit 1 is the number system character, which is always zero when printing zero-suppressed UPCs; digits 2, 3, 4, 5, and 6 make up the manufacturer's ID number; digits 7, 8, 9, 10, and 11 are the vendor's item number(s); digit 12 is the check digit. However, only seven human-readable numbers appear when printing zero-suppressed UPCs.

Interleaved 2-of-5 (I 2 of 5) See Fig. 21-50(*b*).

- Incorporates numeric characters only.
- Can be of variable length, but must have an even number of characters.
- Common applications include warehousing, product/container identification, general industrial, and automotive.
- Often used in UPC Shipping Container Code formats.
- Quiet zone is ten times the width of the narrow bar.

The Interleaved 2-of-5 bar code is a bidirectional, continuous, self-checking numeric bar code. It uses a series of wide and narrow bars or spaces to represent each character, and each symbol employs unique Start and Stop elements.

The symbology requires an even number of characters to be interleaved together. The bars represent data characters occupying the odd positions, and the spaces represent characters in the even positions. Additionally, each data character must be composed of five elements, two wide and three narrow. Character pairing begins with the most significant digit (left-most digit) and continues two at a time until all characters are used. The Start element consist of two narrow bars while the Stop element combines a wide and narrow bar.

Code 128 See Fig. 21-50(*c*).

- Employs alphanumeric characters.
- Can be of variable length.
- Common applications include general industrial, inventory control, and retail container marking.
- Often used in UCC/EAN Serial Shipping Container Code formats.
- Quiet zone is ten times the width of the narrow bar.

This code has 128 characters. Like Code 39, Code 128 offers variable-length symbols. But at the same time, Code 128 is more compact.

Code 128 allows the user to encode any character found on a CRT keyboard, including the control characters. This gives the user more encoding versatility than previously possible in an industrial bar code.

Code 39 (3 of 9) See Fig. 21-50(*d*)

- Incorporates alphanumeric characters.
- Can be of variable length.

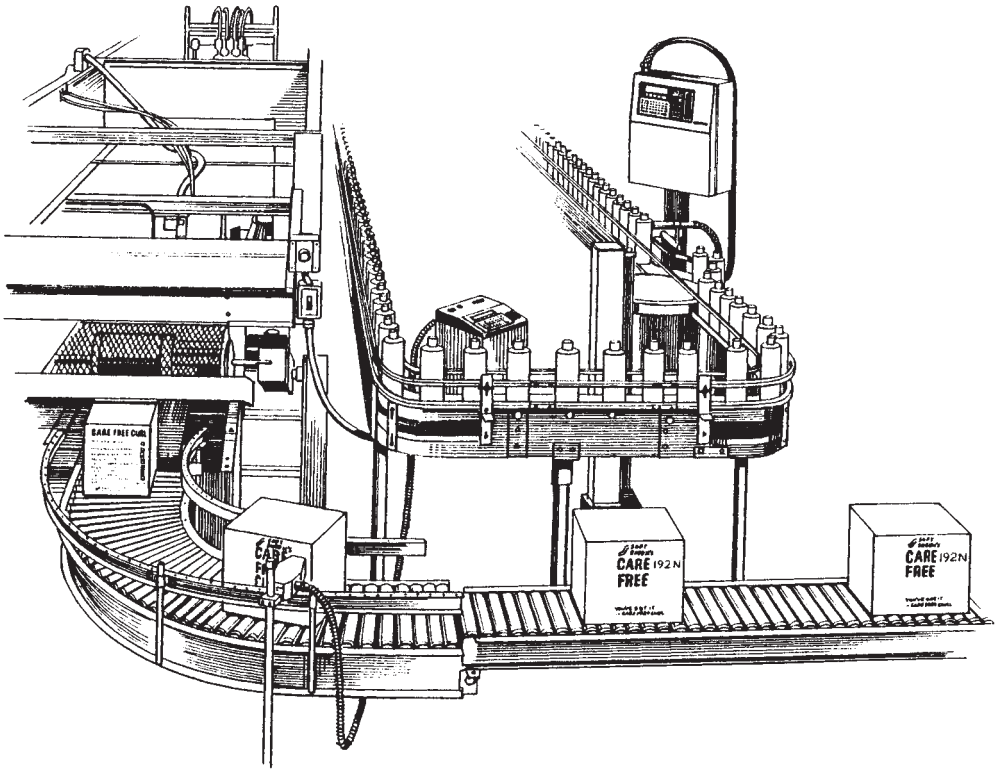


FIG. 21-49 Application of a noncontact ink jet printing system used for coding plastic bottles and corrugated fiberboard cartons. (*VIDEOJET™ shown, courtesy of VIDEOJET Systems International, Inc., 1500 Mittal Blvd., Wood Dale, IL 60191-1073.*)

- Check digit is optional but normally not used.
- Common applications include LOGMARS (Department of Defense), GSA, AIAG (automotive), general industrial, and HIBCC (health industry).
- Quiet zone is 10 times the width of the narrow bar.

The 3 of 9 bar code is a variable-length, bidirectional, discrete, self-checking, alphanumeric bar code. Its data character set contains 43 characters: 0–9, A–Z, -, ., $, /, +, %, and space. Three of the nine elements are wide and six are narrow. A common character (*) is used exclusively for both a Start and Stop character. The Start/Stop characters must be included in every bar code. It's the Start/Stop pattern that allows symbols to be scanned bidirectionally.

Code 39's flexibility to encode both text and numbers has contributed to its widespread use.

PDF417 See Fig. 21-50(*e*)

- Self-checking, two-dimensional bar code.
- Encodes up to 810,900 different character sets and/or interpretations, plus 256 international characters and binary data.
- Allows for bidirectional scanning.
- Symbology includes a Start/Stop pattern, left/right row indicators, and data codewords.
- Quiet zones are two times the *X*-dimension.

PDF417 is a multirow, continuous symbology capable of encoding large quantities of information. It's just what its name suggests—a Portable Data File.

Being one of the first two-dimensional bar codes, the symbology has not yet been standardized by any industry. However, it is being considered for coding shipping manifest information.

The symbology can vary in height and width because any number of rows of information (from 3–90) can be stacked vertically, plus a varying amount of data codewords (from 1–30) can make up the length.

Each PDF417 bar code also incorporates two parity-check codewords, which act as the symbol's error-correction code. The codewords carry out the same functions as check digits in other bar codes.

PDF417 is able to condense so much information into such a small space that it could soon prove to be one of the most flexible bar code symbologies around.

Where products are sold at retail to consumers it is necessary to have a Universal Product Code (UPC) printed on its label. The Universal Product Codes are assigned by the Uniform Code Counsel, 8163 Old Yankee Road, Suite J, Dayton, Ohio 45458. With the bar coding system, the information which is most meaningful to its user can be represented. This can include numeric and alpha (word) representations.

The economic incentive behind the development of the universal product code to allow for automated checkout, has resulted in the development of a whole industry infrastructure which supports bar coding. Automatic reading of bar codes can be done with fully automated systems with the reader as part of a conveyor line, where it reads the bar code from packages as they pass by on a conveyor. Simple systems consist of a handheld "wand" which a person points at the bar code and the code is read. Once read, the bar code analog is then processed by computer which then translates the bar code into the desired information. Such information can include product identity, package size, date of manufacture, manufacturing site, manufacturing process unit, and any special information that applies to the product, such as whether it needs specialized storage conditions, whether it is a hazardous material, and whether it has a shelf life. In Fig. 21-50, (*e*) is a schematic for a bar code system which shows both automatic and manual reading, the translation into useful information, the printing of reports, and the activation of sorting machinery. Two texts having detailed information are: *A Guide to Bar Coding* published by Bar-

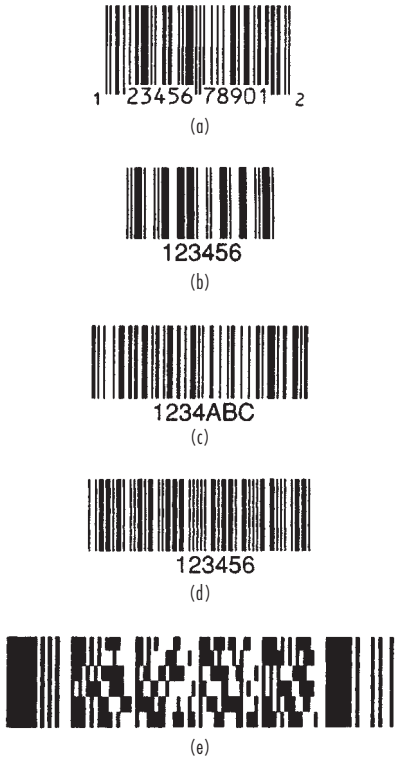


FIG. 21-50 Bar code designs. (*Courtesy of Weber Marking Systems, Inc.*)

coding Systems, Inc., and *Handbook of Bar Coding Systems* by Harry E. Burke. Both are available from the Packaging Book-Store, Institute of Packaging Professional, Herndon, VA 22070. A very good summary of bar codes is the booklet "How to Stay on Top of Bar Codes," by Weber Marking Systems, Inc., 711 W. Algonquin Rd., Arlington Heights, IL 60005-4457, 708-364-8500.

Package Inspection A more critical part of packaging operations is package inspection. In the past this was largely carried out by people, under the heading of "quality control." With the increases in output of typical packaging lines the inspection task becomes greater than the human person is able to accomplish. Several important electronic techniques have been developed which allow for graphic inspection of a number of packaging variables and the rapid rejection of those which do not meet an established standard, and with the passing of those which do. One notable variable is the accuracy of weight or fill volume. Automatic check-weight systems handle all of these. In the case of a product sold by volume a machine-vision system can determine whether the liquid level, in a bottle for example, is at the proper level. Labeling is another variable which has assumed critical importance, especially for products which are regulated by the U.S. DOT or the FDA. Again, machine-vision systems are able to scan each label to be sure that it is correctly applied and that the text is correct for the product being packaged. Metal detection in a product and/or package can be accomplished with several techniques with an x-ray able to detect particles as small as 0.01 mm at high line outputs. Leaking packages can be detected at high speed with helium leak detectors. Figure 21-51*a* shows the installation of machine-vision inspection systems on a typical integrated-packaging line packing tableted products in glass bottles. Figure 21-51*b* shows an X-ray inspection system designed specifically for packaging line use.

Packaging-Line Integration The matching and balancing of all components in a given line so that the line will perform as designed is known as **packaging-line integration.** Computer simulation aids in this integration by allowing test cases of "what if" to run. By defining all conditions under which a line may be expected to function, simulation allows rapid determination of those conditions it can handle, those it cannot, and the quantitative degree to which it can. An example of an integrated line for packaging a tableted pharmaceutical is shown in Fig. 21-51*c*. This line includes inspection by machine vision at critical points and is computer directed and controlled.

Robotics The introduction of **robotics** has given a new dimension to packaging in that it is now possible to do repetitive tasks with speed and accuracy at notably lower cost than if done by people. The manufacture of robots is well established with corporations of substantial resources providing a quality product with continuity of service, supply, and software support. There is also a specialty industry which is available to supply both accessory hardware and software which are custom designed to handle specific user situations. Economic analysis needs to be done before making the decision as to whether to automate using robots, fixed automation, or the labor of people aided by work aids.

There are two principal classes of robots. One type involves a **fixed position** for a central control and manipulator unit, illustrated by Fig. 21-52. This type of device is particularly useful where a repetitive motion is required, such as taking a package component from one position and then rapidly and accurately placing it in another position. The value of the robot increases when there are more than one downstream positions and when sorting must be done. The capability of this type of robot can be further expanded by having a manipulator at its pickup point which also can function in an X-Y-Z axis basis. This permits the device to perform relatively crude tasks such as picking up a component, orienting it, and then moving it to the desired place and precisely positioning it in the X, Y, or Z planes. The term **package components** can mean any part of the package itself or the product which is to be packaged.

A second type, generally regarded as being more versatile than the fixed-point robot, is the **gantry robot.** This device also offers capability of the X, Y, and Z directions. Programming is usually more simple for the gantry than for the fixed-position robot. The gantry robot can also use a manipulator at its pickup and discharge points. This often is as simple as a clamp or a device that has its own X-Y-Z degrees of freedom. Figure 21-53 gives an example of the gantry-type robot that is used for a wide variety of packaging activities, such as palletizing.

A robot often can be economically justified when the task of doing a certain packaging operation is analyzed in detail. For example, the palletizing of the fiber drums can be accomplished by human labor but work aids would be necessary in order to have acceptable production rates, reasonable operator fatigue, and a safe working environment. When the work aids are considered and their cost determined, the additional cost for providing robot capability is often of a small magnitude, which justifies its use to replace human labor.

Another reason for considering the use of robots is the availability of people who are willing to do the hard, manual, repetitive tasks which go with much of the packaging in the chemical industry. In the United States, the cost of such labor—if at all available—can often justify the use of robotic equipment. There are many examples where a single operator controls an entire production and packaging operation where robotics do all of the manual tasks. The robots are under the direction of their software. The operator is often a person who has at least an associate in science degree from a county college. Programming language used for robots is becoming more standardized. This allows robotic equipment to be reused many times after the original operation has been abandoned. It is not unusual to see either a gantry or a fixed-position robot reprogrammed and reequipped with new pickup members, doing an entirely different task than the one it was originally purchased for. One example is a system of a tabletop gantry-type robot used originally in an assembly operation for placing spots of adhesive at precise places on a matrix. After that project was completed the robot was reprogrammed and reused on a packaging line where it places large capsules in blister packs. The investment required for reuse of this robotic system was approximately 25 percent of the cost of a new system. There is much to recommend considering the use of robotics for the packaging activities of the chemical and pharmaceutical industries.

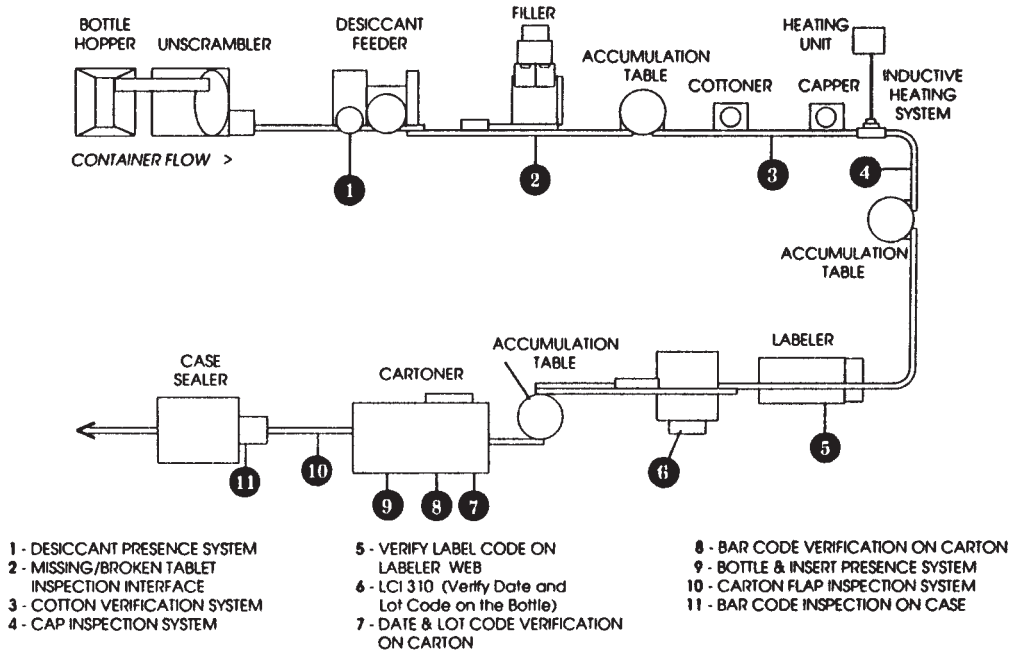


FIG. 21-51*a* Inspection system for an integrated-packaging line packing tablets into glass bottles. Machine vision, bar code technology, and sensor technology are linked together by a supervisory system. (*Courtesy of AGR International, Inc., Butler, PA 16003.*)

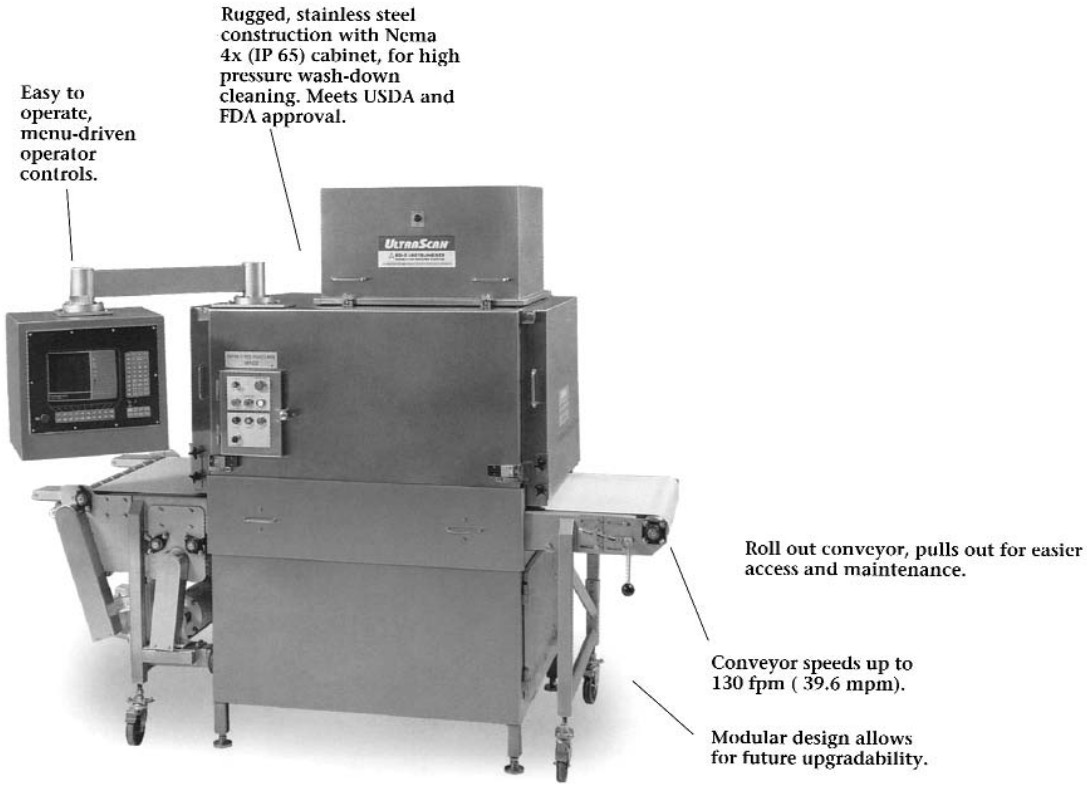


FIG. 21-51*b* An X-ray system for detecting foreign matter in packages. (*Courtesy of EG&G Instruments, Inspection System Division, Oak Ridge, TN 37830.*)

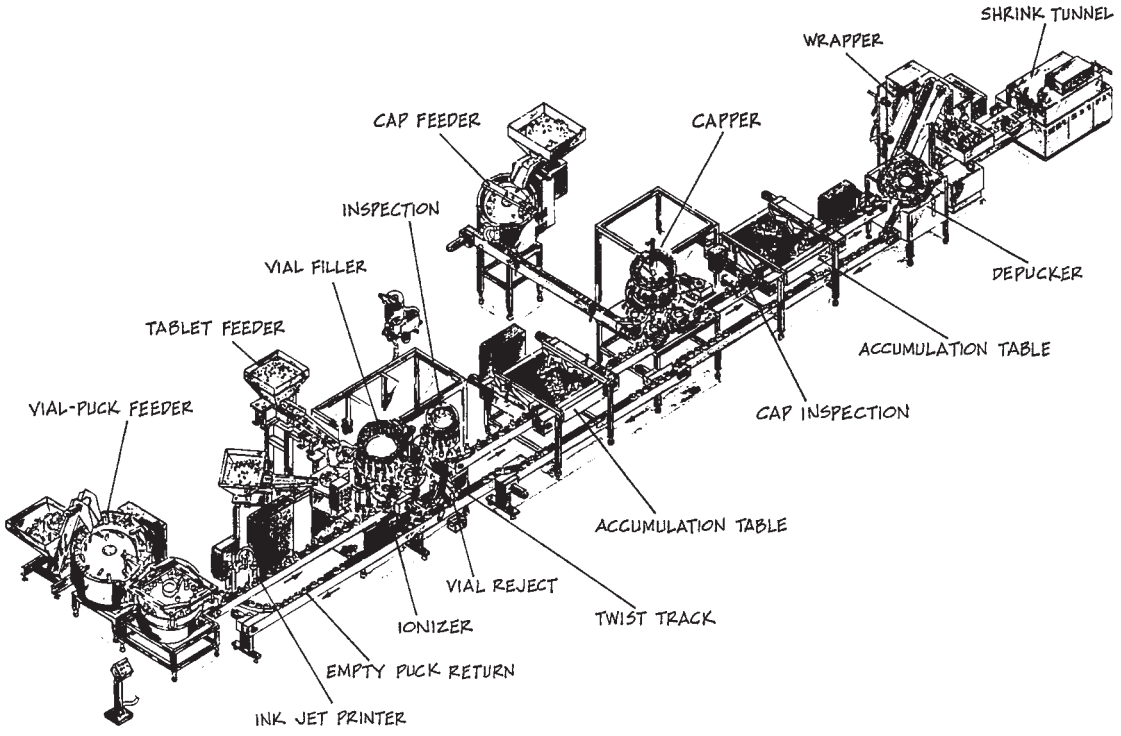


FIG. 21-51c An integrated-packaging line for a tableted product in glass vials (bottles). Machine vision inspection systems check key variables. (*Courtesy of Pharmaceutical & Medical Packaging News, Paoli, PA 19301.*)

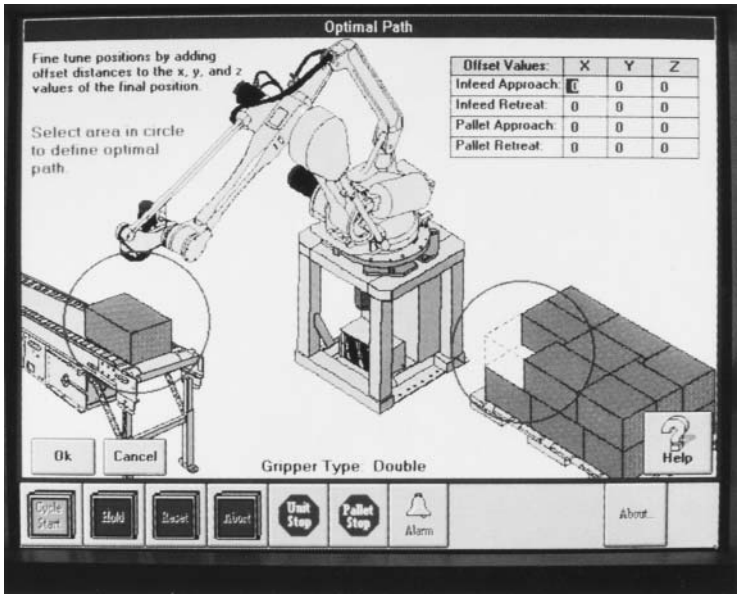


FIG. 21-52 Fixed-position robot used for palletizing of corrugated fiberboard cartons. Robot is integrated with a personal computer using WINDOWS™ graphical-user interface. (*Courtesy of FANUC Robotics North America, Auburn Hill, MI.*)

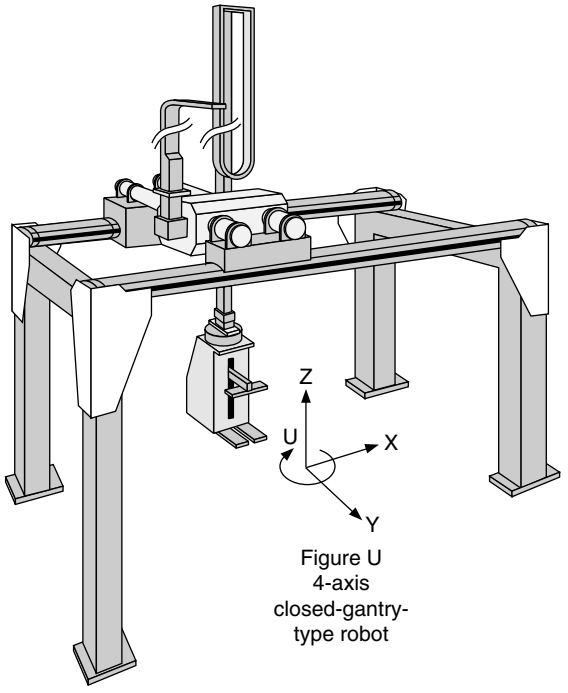


FIG. 21-53 Example of gantry-type robot having 4 axes which would be used for palletizing cartons or bags. (*Courtesy of C & D ROBOTICS, A Division of Ohmstead, Inc., Beaumont, TX 77701.*)

PACKAGE HANDLING AND STORAGE

Warehouse Requirements Finished packages of the chemical industry are usually bags, drums, pails, or cartons (the last-named containing smaller units). Equipment for package handling and storage may be grouped into three main performance categories: (1) from packaging to pallet-unit loading, (2) from pallet-unit loading to storage or shipping, and (3) from storage to shipping.

The trend has been to the use of decentralized warehouses, with less and less finished product being stored at the producing plant. A typical plant inventory consists of 2 to 3 days of production, but at stocking points the inventory may amount to as much as 15 to 30 days. Although high inventory turnover is desirable, the variety of product grades and specifications often leads to longer storage times. Because of this, storage equipment and related conveyors are available to permit either a high velocity of product movement in and out of the plant warehouse or a virtually static one.

Mechanical handling of products in warehouses began with the forklift truck and pallet combination. Since warehouses had no moving equipment, pallet loads were set on the floor or placed on top of one another. Although this procedure is still practiced, loads now move into a storage-rack system, which permits storing pallet loads in vertical columns that make fuller use of the volume or height of the warehouse. Conveyors are also used to carry the pallet loads to storage, retrieve them, and send them to shipping. Forklift trucks are usually involved in all these movements.

Package-Handling Systems The **control of package-handling systems** may depend on simple motor starters, on interlocked relays with photocell control, or on computers. Solid-state controls are finding much application in the last two systems.

A second type of control required is that of the package or pallet itself as it is handled by conveyors and other equipment. This handling may consist of right-angle transfers in a vertical lift or of a set of restrainers on the sides of a belt conveyor.

System Analysis The choice of a specific handling system must take into consideration trade-offs that can be made among different types of equipment and between people-operated and -controlled equipment and automation. A disadvantage of automation is the high cost of specialized maintenance required, which can cost annually between 5 and 10 percent of the original equipment cost and sometimes more. New technical skills are also often necessary.

Factors that enter into any economic analysis of handling-warehousing systems are (1) expected mechanical and economic life of the system; (2) annual maintenance cost; (3) capital requirements and expected return on investment; (4) building-construction cost and land value; (5) detailed analysis of each work position (to determine trade-offs of labor and equipment; expected future costs and availability of labor are important); (6) relation of system control and personnel used in system (trade-offs of people versus mechanical control); (7) type of information system (computerized or manual); and (8) expected changed in product, container, unit pallet loads, and customer preferences during the life of the system.

Forklift Trucks The backbone of most in-plant handling systems in the chemical industry is the forklift truck. Available in capacities ranging from 1 to 50 tons, the most commonly used are 1-, 1.5-, and 2-ton vehicles, with the 3-ton unit occasionally being used (Fig. 21-54). The trucks are usually powered by internal-combustion engines that consume liquefied petroleum gas (LPG) or by electricity by means of storage batteries.

With internal-combustion engines, automatic transmissions are frequently used; these are easily justified when vehicles must make many moves during the day. Smooth as is the control afforded by automatic transmissions, it is nevertheless inferior to that provided by electric trucks, especially those with solid-state controls. Gasoline and diesel power are also used, but mostly for outdoor equipment and very-heavy-duty units.

The lift-truck industry is competitive, with innovations being introduced frequently. Competent sales and service are available at low cost from most manufacturers or their dealers. Application sales engineering (a very worthwhile service) is generally supplied at no cost.

The many **options available** for lift trucks fall into two classes: vehicle specialties, which include controls, transmissions, guards, etc.; and accessories, which are devices that handle specific types of loads (Fig. 21-55). Included in this second category are high-lift masts, up to 7 m (24 ft); handling attachments for circular products, such as drums and roll goods; attachments such as carton clamps; and the fork side-to-side shifting mechanism.

Worthy of particular notice among accessories is the **side shifter** that is used to move trucks horizontally, about 100 mm (4 in) from side to side. The modest cost of this feature is returned in a few months' operation through reduced handling time, maintenance, and product damage. The driver first positions the truck approximately in front of where the load is to be set down and then makes the final horizontal adjustment by means of the side shifter. Without this mechanism, two or three maneuverings of the truck are necessary, with the load never quite being placed in the ideal spot. Correct positioning is important for pallet loads, which should be placed as tightly together as possible.

Lift trucks are available to meet a variety of **clearance restrictions.** Noteworthy is narrow-aisle equipment. Another accessory worthy of consideration is the multilift mast, which permits lifting loads over 3.7 m (12 ft). Of special importance in specifying any mast is that it will clear the various door openings it must enter, which includes those of trucks, railcars, and buildings. To meet most conditions, the collapsed height of the mast must be 2235 mm (88 in). An ideal lift truck for chemical-plant distribution warehouses would have 2000-kg (4000-lb) capacity; electric (battery) propulsion; solid-state controls; power steering; Trilift mast, up to 4.9 m (16 ft) [2235 mm (88 in) collapsed]; side shifter; operator guard; solid tires (except for outside use); and adjustable forks.

Exceptions to the preceding requirements would apply where explosionproof equipment is needed; building ceiling heights are such that the standard 3.7-m (12-ft) lift is all that will ever be needed; and loads will never exceed 1 to 1.5 tons. Safety requirements for lift trucks are mandated by OSHA, by NIOSH (National Institute of Occupational Safety and Health), by State Depts. of Labor, and often by individual company standards. Among these requirements are backup-movement signals, seat belts, overhead framework for pro-

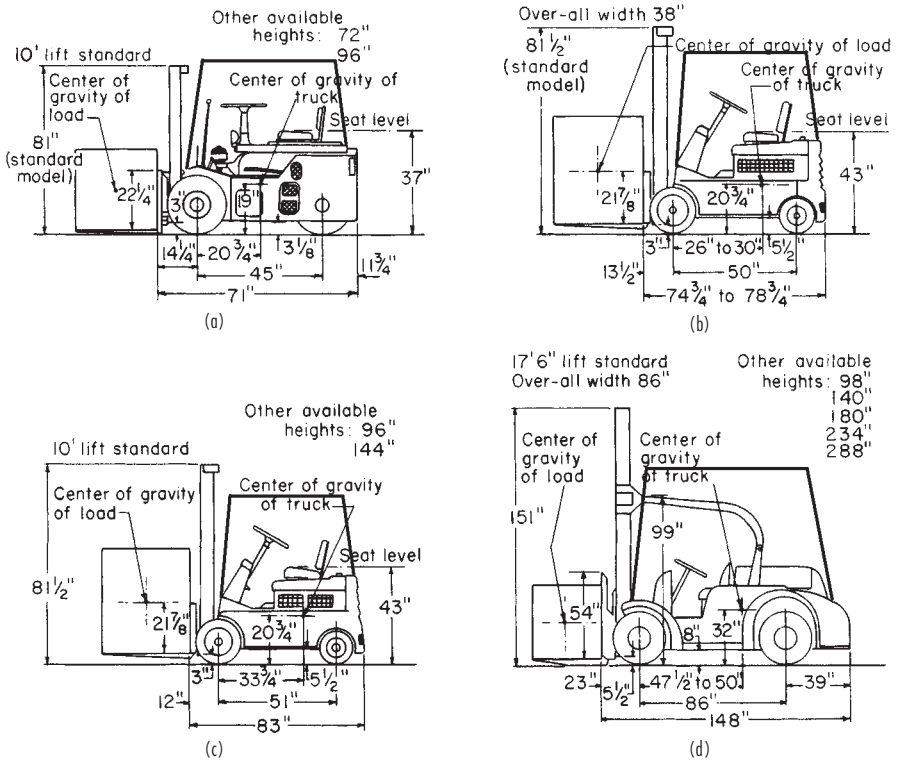


FIG. 21-54 Dimensions of representative forklift trucks. (*a*) 1000- to 2000-lb capacity. (*b*) 3000- to 4000-lb capacity. (*c*) 5000-lb capacity. (*d*) 10,000- to 12,000-lb capacity. Multiply pounds by 0.4536 to get kilograms; multiply inches by 0.0254 to get meters. (*Hyster Co.*)

tecting the operator from falling items, flashing lights, and two-way radio transmitters. Driver training is also mandated. A prominent training program is that of the National Safety Council. It includes video instruction, home workbooks, written and oral tests, and a demonstration of competency in operating an actual lift truck.

Capital investments in forklift equipment vary with specifications. Table 21-27 compares the cost of the electric-propulsion truck just described with an LPG-operated alternative. The operating cost is primarily for energy, with electric consumption being cheaper than liquid fuels.

Maintenance on gas trucks is also higher than with electric vehicles. About 5 percent annually of the initial cost applies to internal-combustion equipment, and about 2 percent annually to electric. A special feature on electric trucks with solid-state controls is the use of modules or circuit boards, which can be replaced as units and rebuilt at the factory. Typical maintenance costs for trucks operating five 8-h shifts per week are in the order of $3.15 per hour for gas vehicles and $1.78 per hour for electric ones. Under these conditions, energy costs are typically 9.3 cents per hour for gas trucks and 5.1 cents per hour for the electric units.

The **straddle truck,** designed for lifting bolsters with heavy loads or materials such as structural steel, is also finding application in handling van-type containers of packaged goods. For example, it can straddle a flatcar, pick off a van container, and deposit it directly on a truck-trailer rig. It can also be used for loading railroad flatcars and even oceangoing vessels. It is just one of many special pieces of mobile equipment available for special handling problems.

Slide Conveyors Simple gravity slides and spiral chutes, while not technically conveyors, are widely used with conveyor systems or as separate units for lowering materials from one floor to another. They are low in cost and require little floor space if slopes are held at fairly steep angles. However, they must be used only after a careful study of possible damage to containers from bumping either together or against the sides of the chutes or slides. Enclosed units are available for outside operation, and fire doors can be provided to meet requirements of local building codes. Multiple-blade chutes may be used for service to several floors, with separate inlet and outlet points. Blades may be lapped and riveted to eliminate the possibility of containers hanging up on exposed edges. Flight sections may also be flanged and bolted together.

Speed of containers sliding down a spiral may be controlled by the pitch of the spiral or by banking the outer or inner edge of the blade. Banking tends to throw the container to one side of the blade, thus varying its total travel distance. While usually fabricated of steel, blades may be specified in different materials, as required by specific applications.

Because of the steep pitch required, **slides** are limited in application. They are most commonly used to bridge the gap between roller-conveyor systems on two floors, because the roller conveyor can take the container off the slide rapidly and eliminate or reduce the chance for collisions. Slides may also be used when containers can be chuted from an upper floor to a manually loaded carrier. The use of several rollers at the feed point is recommended for easy delivery to the sloping section. If the drop is short and containers light, a roller cleanout will prevent backup of containers on the slide. The slope of gravity slides is a function of container weight, size, and friction characteristics and should be selected with care to be sure that containers do not move either too swiftly or not at all. Slides usually use flat steel sheet.

Gravity Wheel Conveyors These can be used as pusher units set horizontally or inclined for gravity flow. They are highly standardized and are usually sold in 1.5- or 3-m (5- or 10-ft) sections; special lengths are available at extra charge. Since wheel conveyors give what is essentially "point" support to containers, it is generally recommended that at least six wheels be located under the load at all times.

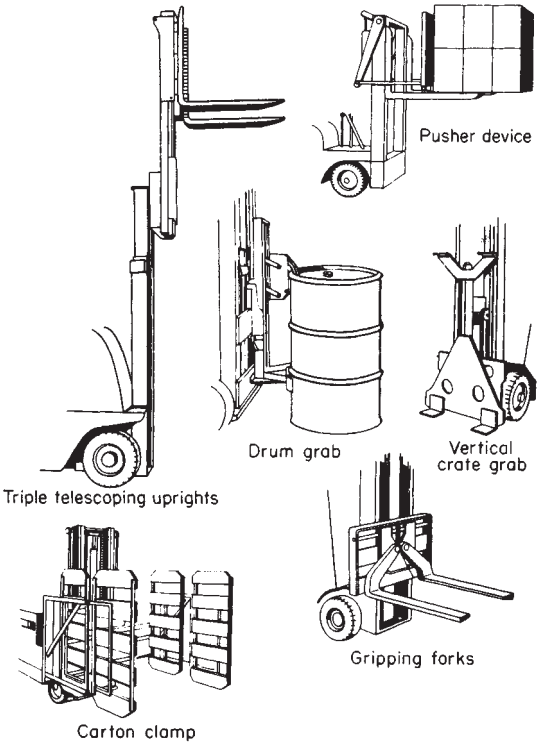


FIG. 21-55 Various types of fork-truck attachments.

Thus wheel arrangement is dictated by the smallest container that the line will handle. Only flat-bottomed containers can be handled on wheel conveyors, with the exception of fairly stiff-walled bags, which handle satisfactorily. This is due to the fact that the separate roller supports tend to pull the bag wall taut and flatten it out. Roller conveyors, on the contrary, tend to ripple the bag surface and prevent its movement. Wheel conveyors may also be specially designed for handling smooth-walled cylindrical shapes.

Wheels are available in a number of different designs, including variations in contour and material in contact with the container. Rubber or plastic tires are not uncommon. Through shafts may be used, with several wheels mounted on each shaft; stub bolts with a single wheel may be mounted to the side frame, or short shafts supported by bent bars may also be used. Wheel conveyors are generally used on lighter loads, and although manufacturers may offer widths up to 915 mm (36 in) or more, the smaller widths [up to about 457 mm (18 in)] are generally standard. Load ratings are generally given as the total uniform load which a standard section will support.

Since wheel units are relatively light, they have relatively low inertia, and loads may be started and stopped quite easily. In addition, wheel bearings are designed with loose tolerance to reduce starting friction. Metal plates or projecting hardwood slats are commonly used as stops on conveyor lines. Special hinged sections for passage of personnel through the conveyor line are available, and standard supports from floor or ceiling are recommended. Wheel-conveyor units are widely used for live storage, and special telescoping units are available for extension and retraction to meet variable conditions. Wheel conveyors are sometimes powered by a pressure belt or other methods but are most widely used as pusher or gravity lines. They are adaptable only for end discharge or side discharge by lifting, since the individual rollers tend to grip the container and prevent its sliding off the line at right angles to direction of travel.

Roller Conveyors Gravity rollers are considerably heavier than the wheels on wheel conveyors, and the weight is concentrated at a greater distance from the shaft centerline. Hence, roller conveyors have a greater inertia; they are harder to start and harder to stop, require more slope than wheel units, and on long runs tend to speed up containers at an accelerating rate.

Spiral-roller units are usually equipped with tapered rollers to compensate for the difference in distance traveled by the inner and outer edges of the container. Tapered rollers are also used on curved sections of ordinary roller-conveyor lines.

Rollers are available in a wide **variety of constructions,** with tube ends either bored or formed to take the bearing insert. Bearings may be plain, with nylon rapidly becoming the most popular material for this type. Ball bearings are probably most common and are available with a variety of seals, or the bearing may be left unprotected. Lubrication fittings may be provided on a drilled shaft, or bearings may be prelubricated and sealed for life. Roller shafts are usually nonrotating and may be cut from hexagonal stock to fit a similar opening in the side frame, or they may be round with ends milled flat to prevent turning. Rollers may be mounted in side frames in a variety of ways, above the side frames when containers are to be slid off the line or below when there is danger of the containers falling off.

Gravity roller conveyors can handle containers with protruding edges, i.e., steel drums, which is one of their advantages over wheel conveyors. However, they are not generally suitable for bags since the sides tend to sag between supports and prevent forward motion.

As with gravity wheel conveyors, roller units are highly standardized and auxiliary equipment is available for supporting the line from ceiling or floor. Many special rollers are available for retarding containers if speed becomes too great for safe handling. Switches, brakes, hinged sections, spurs, and frogs are also available.

Roller conveyors are quite frequently **powered,** the simplest method being use of a pressure belt in contact with the lower surface of the rolls. A special ripple belt with raised pads is capable of starting up the load but does not build up excessive blocked pressure if the line fills up. Other similar drives are available, with varying degrees of control over the applied power. Most expensive of the powered roller units are those in which each roll is equipped with V-belt or chain drives. Pusher bars suspended from overhead chain conveyors may also be used to move containers along a roller line.

One of the most important control devices on roller-conveyor lines is the escapement mechanism which allows containers to be released from a line individually. Powered escapement mechanisms are commonly available on highly mechanized systems. Their main function is to space out the containers so that they can be handled as discrete units.

Flat-Belt Conveyors These powered conveyors can lift containers up inclines. With the aid of special belt surfacing, grades may be quite steep. Belts also keep containers spaced out in exactly the way in which they are placed on the conveyor. However, because of the relatively high friction containers cannot be slid off belts by pushing devices.

Belt-conveyor designs use both roller and slider bed supports for the flat belt. The variety of designs available allows proper selection of flat belts for heavy or light loads and for various applications such as carton filling or emptying.

TABLE 21-27 Initial Capital Investment Comparison between Liquefied Petroleum Gas and Electric Forklift Trucks of 2-Ton Capacity*

Item	Liquefied petroleum gas	Electric
Basic truck	$40,000	$46,000
Automatic transmission	$ 1,300	
Solid-state controls (standard)		
Trilift mast, to 4800 mm (189 in)	$ 4,500	$ 4,500
Side shifter	$ 4,500	$ 4,500
Power steering (standard)		
Solid tires (standard)		
Storage battery and charger		$16,000
Total	$50,300	$71,000

*Based on 1995 prices (U.S. dollars). Initial inventory of repair parts is not included in these prices.

Chain Conveyors These devices for handling containers are available in either roller-chain designs or less costly types. There is a variety of **slat conveyors** that use both single and double strands of roller chain, as well as a slider type using cheaper chain. In general, slat chain conveyors are used only on loads which are too heavy for economical handling by belt, roller, or wheel units or which have odd shapes not suitable for roller or wheel units. They are particularly adaptable to pallet handling, as are simple open strands of chain with flat-surfaced attachments.

The most commonly used warehouse chain conveyor is the **tow chain.** Chain may be mounted overhead or in the floor, and trucks being towed can be designed for automatic detachment at a specific point. While the overhead chain is often used and is usually easy to support from structural members in the ceiling, the in-floor chain is probably most common. Automatic disengagement is possible should trucks encounter an obstruction or accidentally strike warehouse personnel. The two-chain conveyor is, of course, most economical when large tonnages are moved over a fixed path.

Chain-type **elevators,** such as arm and tray units, are commonly used for drums and barrels. Slight gravity runs at feed and discharge allow these units to roll on and off the conveyor easily and without special equipment.

Elevators Cable-type elevators are usually selected for heavy loads such as full pallets or large containers. They can be made fully automatic and are able to serve many floor levels. The use of properly designed elevator systems is often the only economical solution to multistory-plant problems.

Conveyor Accessories These may be divided into two groups, those which act on the container and those which are acted on by the container. In the first group are such items as deflectors, palletizers, pushers (powered by fluid, air, or mechanical linkage), upenders, sealers, staplers, and similar devices. In the second group are such items as electric eyes for counting or identification via printed or color codes, check weighers, mechanical counters, and other devices contributing to automatic conveyor-line operation.

Automatic Palletizers These machines receive packages from production by conveyor. The packages are then arranged in tiers, and the tiers are placed on pallets. The mechanism to accomplish this consists of package-handling conveyors, package-moving stops, rams, etc.; a package-tier-pattern assembly plate; an empty-pallet-handling conveyor and elevator; a filled-pallet-handling conveyor; and electrical regulators to control the tier-pattern formation. Automatic pallet loaders can handle 40 to 80 packages per minute, or one to two pallet loads. Capital investment is about $225,000 for the basic machine, not installed. Semiautomatic operator-directed palletizers capable of handling 10 to 20 packages per minute are available; they cost approximately $95,000, not installed (1995 prices).

Package-handling systems can be designed to handle almost any situation of package type, packaging machine, and warehousing-transportation requirement. Figure 21-56 shows a typical bag-handling

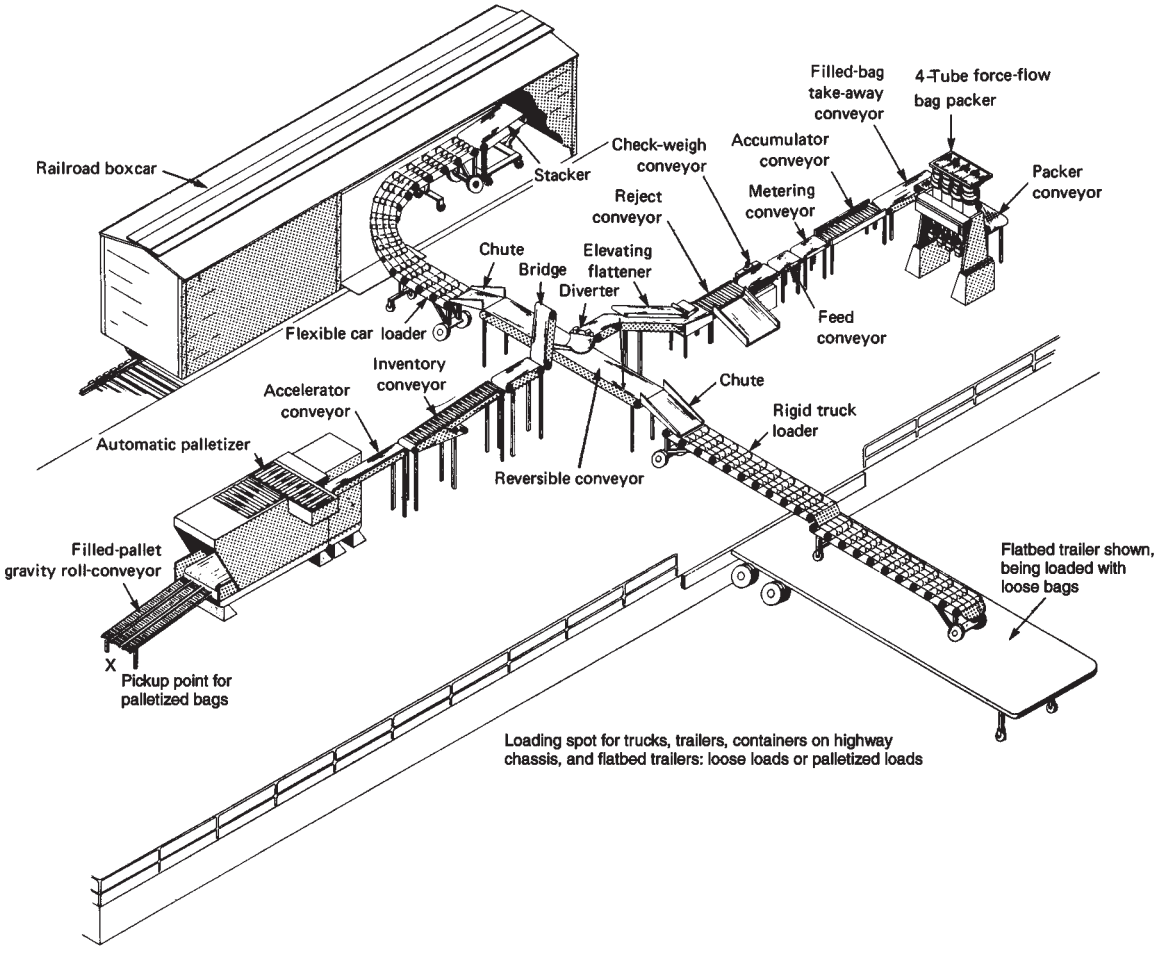


FIG. 21-56 Typical four-tube force-flow valve-bag packer with automatic palletizing and truck- and railcar-loading facilities. (*Courtesy of Stone Container Corp.*)

system in which both palletized loads and loose bags are handled. A system of this type can handle thirty 25-kg (50-lb) bags per minute. Figure 21-57 shows a system using the pinch-bottom-type open-mouth bag. Such a system can handle ten 25-kg bags per minute. Performance data for both examples can be found in Table 21-26.

Storage of Packaged Items The inventory needed to support a given sales level is increasing in quantity as well as in the number of places where inventories are maintained to provide better service. Since a major portion of the chemical-process industries is located in urban centers where space is extremely valuable, efficient ways of storing packaged inventory have become very important. A similar situation exists when inventories are maintained at production plants. Here, space may be more readily available than in urban locations, but there is the question of whether to use the space for storage or for processing. These situations have led to the development of the storage-rack concept.

Storage racks permit storing pallet loads of packages vertically as well as horizontally. Most pallet loads can be tiered two or three pallets high, with one resting on top of another (provided the packages are able to withstand the weight of the pallets above). Because the racks bear the pallet weight, stacks six to eight and even more pallets high are possible. Forklift trucks and stacker cranes are used to place and remove the pallets.

From an inventory-turnover point of view, four major rack-storage systems are possible: drive-in, drive-through, flow, and aisle.

Drive-in racks, which are practical up to a height of 10 m (30 ft), are serviced by forklift trucks. The inventory system required is last-in–first-out (LIFO), which many consider inefficient. Capital investment (installed) for a 5000-pallet rack system is about $90.00 per stored pallet, lift truck not included. Drive-in racks make good use of floor space, having a higher ratio of storage to aisle space than aisle racks.

A typical drive-in rack consists of a steel structure to support palletized goods at the pallet edge, with the center of the pallet unsupported. The space between pallet support members is sufficient to permit a lift truck to drive in to place or retrieve a load. These racks are usually made to accommodate 12 pallets, which are positioned from the service aisle to the end of the rack. Because of the rack, each pallet position has the ability to hold 6 to 8 pallets vertically.

In operation, the lift truck takes the first pallet load and drives to the end of the rack to set down the pallet. With the second pallet, the truck enters the rack with the pallet elevated to permit clearing the support member. This procedure is repeated until the rack is filled. Lift-truck productivity is low because the driver must possess agility and skill to manipulate pallets extended on the truck.

Drive-through racks are similar to the drive-in kind, differing mainly in having lift-truck access at both ends. The main advantage of drive-through racks is that they allow a first-in–first-out (FIFO) type of inventory management. Capital investment, installed, is about $100 per pallet for a 5000-pallet rack structure. In operation, the rack is loaded in the same way as a drive-in rack. The unloading is different, in that removal of pallets begins at the opposite end from the loading point.

Flow racks are similar to drive-through racks in that they are loaded from one end and unloaded from the opposite end. However, the truck does not enter the rack. Rather, each lane in the rack is equipped with a conveyor (roller, wheel, or belt, depending on pallet characteristics) which both supports the pallet and transports it (by

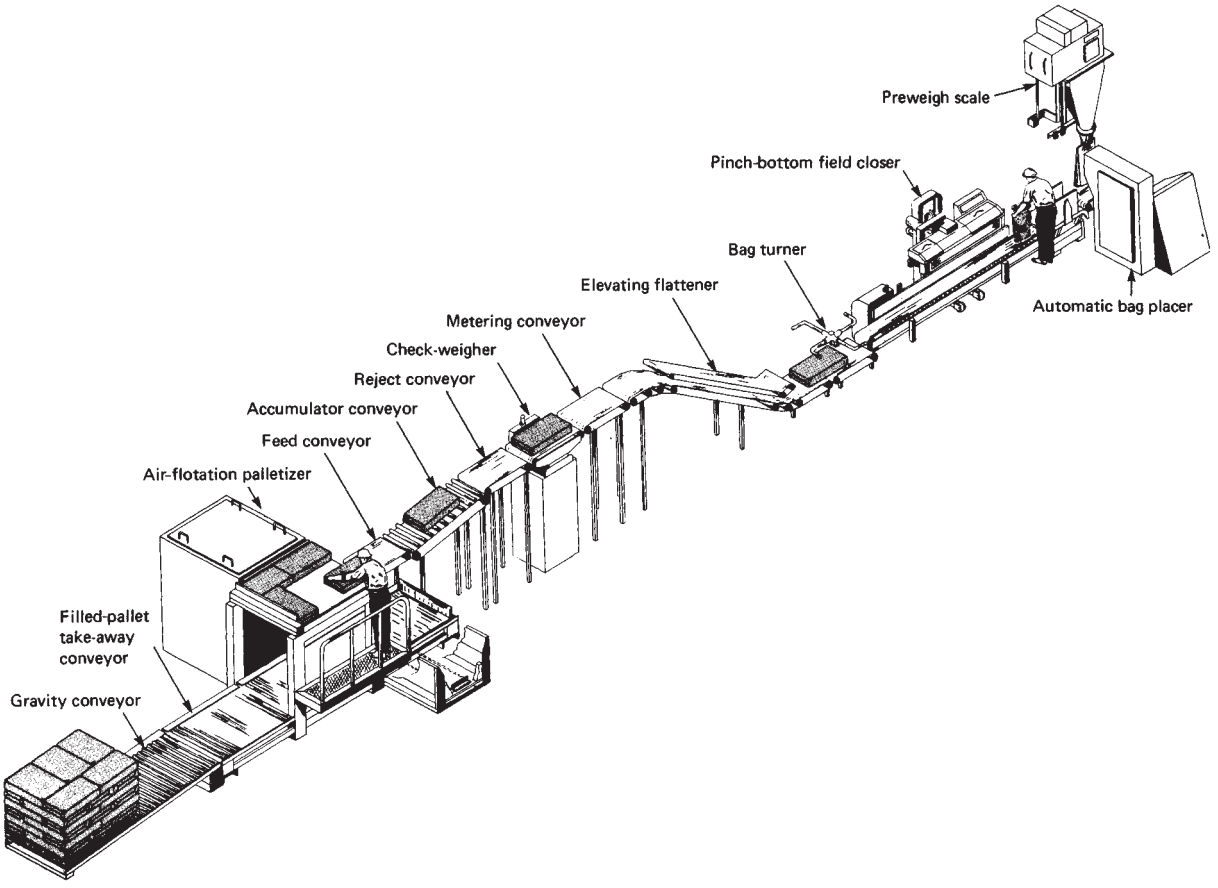


FIG. 21-57 Typical pinch-bottom system with automatic bag hanging and semiautomatic palletizing. Filled bags are handled on pallets only. (*Courtesy of Stone Container Corp.*)

gravity) from the entry point to the discharge end or to the nearest pallet. As a pallet is removed, the remaining ones flow to the removal point. This is a FIFO system of inventory.

The installed capital investment is about $375 per pallet for a 5000-pallet system. A characteristic of drive-in, drive-through, and flow racks is that, at any one point in time, only one product can occupy a given storage lane. Products are not mixed because of the complications that this practice presents in inventory management. In any event, there is seldom any need to mix products in the chemical industry because products are made in lots, blends, etc., and a storage lane is ordinarily designed to accommodate either a complete lot or some fraction of a lot. The result is that the total storage space available rarely is completely used. This is a problem that aisle racks overcome.

Aisle racks, used when there is a rapid turnover of inventory, permit a storage depth of only one or two pallet loads but offer the advantage of instant access to the stored item. Although this requires only a minimum of lift-truck time to store or retrieve a pallet, a high percentage of floor space must be devoted to aisles.

The inventory system needed is FIFO, which is desirable when inventories are subject to obsolescence or deterioration or when they consist of raw materials that fluctuate widely in value. The capital investment for a typical aisle-rack storage system having a 5000-pallet capacity (1 deep) is $65 per stored pallet (this does not include lift-truck investment).

Lift-truck operation is very simple and productive, even at 7-m (20-ft) elevations. Aisle racks can be as high as 30 m (100 ft), but above 7 m stacker cranes are favored over lift trucks because cranes allow servicing high storage at high rates. The installed investment in aisle racks, including a stacker crane, is about $500 per pallet.

Automatic Storage and Retrieval Systems These systems are of increasing importance in the warehousing of chemical products whether they are for consumer or industrial markets. They are comprised of warehouse racks which can be several stories high. These racks are serviced by stacker cranes equipped for palletized handling. Each rack is divided into storage modules. Each module is capable of holding one pallet load of product and has an address which is stored in a process control computer memory. Stacker cranes are under the direction of the process-control computer. Through use of bar codes marked on packages and pallets, products entering the warehouse are identified by such variables as nomenclature, weight, package type, and any expiration date. The entering pallet load is identified by its bar code through use of a laser scanner which picks up the information from the bar code and transmits it to the process-control computer. The computer then directs the stacker crane to an empty storage module which is available and makes a record of the product and its storage location. The stacker crane places the pallet load in the module. The computer verifies this record before the stacker crane leaves the storage module. Stacker cranes often are equipped with an enclosure for a person who can ride the crane and inspect any storage module. This is also used where an operator does order picking, as in the case when single cartons of product are ordered. The term *paperless warehouse* is a very apt description of automatic storage and retrieval systems since they rely entirely on bar code, scanning, and computers, with a minimum of personnel. Pallets for such systems must be accurately made to required dimensions and have sufficient mechanical strength to withstand the repeated handling. Often, metal pallets are used to support wood pallets and their loads. The metal pallets never leave the warehouse, and assure trouble-free operation.

TRANSPORTATION OF SOLIDS

TRANSPORT OF BULK SOLIDS

Originally confined to the shipment of crude raw materials and fuels, the term "transportation of bulk solids" now applies also to manufactured products, which often become raw materials for other industries. In recent years, increasing tonnages of highly processed, finished chemical products have moved to customers in large bulk units. A useful definition of a bulk shipment is any unit greater than 2000 kg (4000 lb) or 2 m^3 (70 ft^3). The containers available range from small portable hoppers of 2-m^3 (70-ft^3) capacity to railroad cars of 255-m^3 (9000-ft^3) capacity.

The choice of shipping in package or bulk depends on market requirements and economics. Products from different sources that tend to have the same characteristics (appearance, quality, price) are usually offered in bulk form. Those tending to be specialties, while sometimes offered in small bulk units, usually are sold in packages. Many products are sold in both ways. A comparison of the costs of typical package and bulk units is given in Table 21-17.

Bulk Containers These containers may be either open or closed. Generally, it is the effect of the weather on the product that governs the choice. High-value materials, such as certain ores, may be shipped in open containers, while relatively low-cost items, such as portland cement, require closed containers. Further influencing the choice of bulk containers is whether deliveries are made by truck, railroad, or water.

When customers maintain small inventories, **truck** delivery is often used, provided the location of the supply point is nearby, usually 550 km (300 mi) or less, and deliveries are frequent. If, however, a user maintains large inventories, deliveries are ordinarily made by **rail.** Other parameters influencing choice are transportation cost; operating costs of supplier loading facilities; customer receiving and unloading facilities; turnaround time for the container and the number of trips made per year (hence, investment write-off per trip); and container-operating cost, exclusive of transportation.

In planning for railroad-car loading or unloading facilities, many dimensional and weight factors must be dealt with. The common carriers that are to serve the facility are usually able to provide technical assistance as to clearances and weights to be handled.

An interesting new concept in planning for finished goods and bulk storage (when rail is used principally for customer delivery) is the use of hopper cars instead of fixed storage bins. Since products are eventually to be loaded into cars, there is much to be saved by avoiding double handling and capital investment. A systemwide analysis often will show this to be the least costly method, especially if there is a policy of minimum finished-goods inventory.

The most important bulk containers are railroad hopper cars, highway hopper trucks, portable bulk bins, van-type (ship) containers, barges, and ships. Factors determining the suitability of any of these containers (after establishing whether open or closed containers are to be used) depend on product physical properties, the most important of which are ease of flow, corrosiveness, and sensitivity to contamination.

Railroad Hopper Cars Hopper cars follow three basic designs: (1) covered, with bottom unloading ports; (2) open, with bottom unloading ports; and (3) open, without unloading ports. Three types of unloading systems are used: gravity, pressure-differential, and fluidized. For the open-type car without unloading ports, clamshell buckets are often used. The car is loaded through ports located on the top of the car. Figure 21-58 shows a common type of covered hopper car.

Table 21-28 gives dimensions of hopper cars and other cars typically used in the chemical industry. Vacuum-pressure systems are used most frequently for unloading covered hopper cars. For certain free-flowing materials, in both covered and open-top hopper cars, shake-out devices are useful.

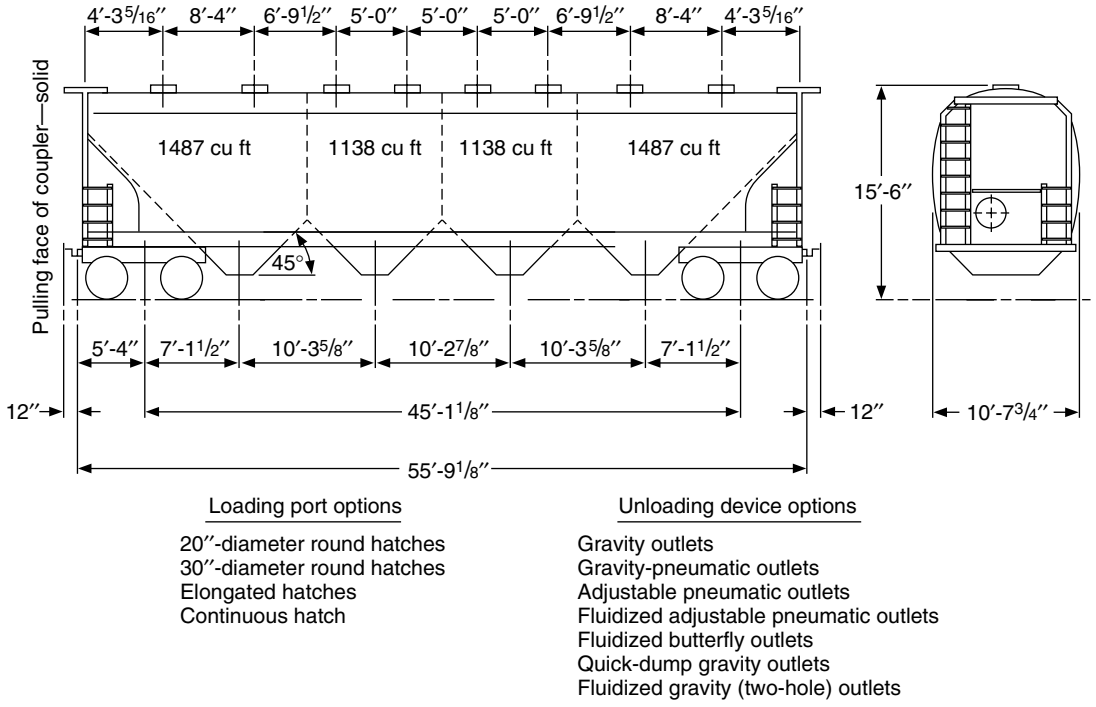


FIG. 21-58 Typical railroad covered hopper car, 5250 ft^3 (148.7 m^3) ACF Centerflow designed for ladings having a bulk density of 42 lb/ft^3 (672 kg/m^3). Load limit 200,000 lb (90,720 kg). Unloaded weight with 20 in (508 mm) loading ports and gravity pneumatic unloading devices is 66,920 lb (33,355 kg). (*Courtesy of ACF Shippers Car Line Division.*) Change dimensions to inches and multiply by 25.4 to get mm. Multiply ft^3 by .02832 to obtain m^3.

Because of the railroad-car shortage that has persisted for many years, boxcars are often used for bulk materials. Lined with suitable materials to prevent contamination and with special bulkheads at each door, these cars are acceptable substitutes for covered hopper cars even though unloading is more difficult. Vacuum conveying wands are used to pick up the material, as are front-end-loader-type vehicles.

Loading of hopper cars and trucks can be done with most types of conveyors: air, belt, screw, etc. When an extremely full loading is required, centrifugal trimmers are frequently used. Available in a range of capacities, they can be engineered for any size of unit, up to a shiphold cargo (Fig. 21-59).

Track hoppers are needed for some boxcar and bottom-dump-car shipments. Since boxcars discharge to one side, fairly light construction can be used for the hoppers, which are located to one side of the tracks. However, for bottom-dump cars, the hoppers must be located on the centerline of the tracks. This requires heavy track girders over a hopper and feeder conveyor pit, but hopper depth must be set to give sufficient angle for material to flow well. Belts or reciprocating-plate feeders commonly carry the material to the bucket elevator.

TABLE 21-28 Typical Railroad-Car Dimensions and Capacities*

Type of car	AAR* class	Nominal inside dimensions, Length	Width	Height	Nominal outside dimensions, Length	Width	Height	Cargo (lading) volume, cu. ft. × 100	Cargo (lading) weight, lb. × 1000
ACF center-flow hopper car	LO				39 ft. 8 in.	10 ft. 8 in.	14 ft. 10 in.	29.7	207
ACF center-flow hopper car	LO				54 ft. 8 in.	10 ft. 9 in.	15 ft. 1 in.	47.0	200
ACF center-flow hopper car	LO				59 ft. 2 in.	10 ft. 9 in.	15 ft. 1 in.	52.5	200
GATX	LO				42 ft. 0 in.	10 ft. 8 in.	14 ft. 4 in.	26.0	140
Airslide hopper car	LO				54 ft. 6 in.	10 ft. 7 in.	14 ft. 6 in.	41.8	192
Hopper car	HT	42 ft. 10 in.	9 ft. 8 in.		43 ft. 10 in.	10 ft. 6 in.	10 ft. 8 in.	27.5	157
Gondola car	GB	41 ft. 6 in.	9 ft. 4 in.	2 ft. 5 in.	42 ft. 9 in.	10 ft. 2 in.	6 ft. 2 in.	9.6	100
Boxcar	XM	50 ft. 7 in.	9 ft. 6 in.	10 ft. 8 in.	55 ft. 2 in.	10 ft. 6 in.	15 ft. 9 in.	51.2	100
Boxcar with DF† equipment	XL	50 ft. 6 in.	9 ft. 5 in.	10 ft. 6 in.	57 ft. 7 in.	10 ft. 6 in.	14 ft. 10 in.	49.5	100

*From Association of American Railroads. Data are given for United States railroads, which do not use SI dimensions. To convert to SI dimensions (millimeters), change dimensions shown to inches and multiply by 25.4. To convert volume to cubic meters, multiply by 0.02832. For weight, multiply by 0.4536 to obtain kilograms.
†Damage-free.

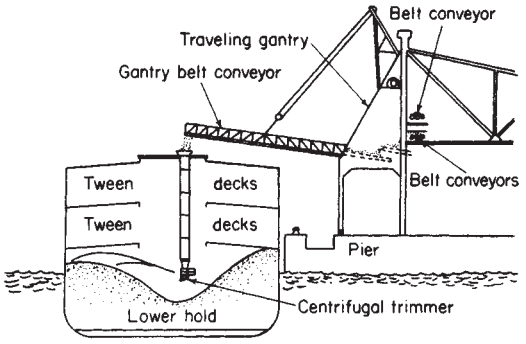


FIG. 21-59 Ship-loading system with trimmer and telescoping chute. (*Stephens-Adamson Division, Allis-Chalmers Corporation.*)

Hopper Trucks These trucks are used to transport by highway a wide variety of materials. Vehicle types range from the open-dumping kind to the closed type. Most common is the type that unloads by pressure differential into its own pneumatic-conveying system, which is temporarily connected to a storage silo. On this type of truck, the unloading of 18,100 kg (40,000 lb) of products takes about 1 h, sometimes less.

The actual weight that the truck can carry in the United States depends on state-highway load limits, which in turn depend on the net vehicle weight and the number of axles on the truck (and tractor, when a trailer arrangement is used). The accepted maximum combined total weight of vehicle and cargo is 36,200 kg (80,000 lb). In some states, this is reduced slightly, while in others it is exceeded.

Of significance is the rapidly developing containerization system used for package cargo. SeaLand Corp. has developed a patented liner device which can be used to convert a cargo container into a bulk carrier. Figure 21-60*a* provides dimensions of typical bulk hopper-truck equipment.

Important in the planning for an installation that is to handle rail and highway equipment are the width, length, height, and turning radius of vehicles that will serve the facility. These dimensions can be easily obtained from carriers as well as from equipment manufacturers. Adequate clearances must be provided for railroad and other work crews. The clearances are often specified in state labor-practice codes.

Movement of railcars and trucks within plants is frequently done by carrier crews. Since, however, plant production schedules and availability of railroad switch crews are often not compatible, many plants provide their own switching service. Specially built prime movers that can operate on both roads or rails are available. Front-end loaders can be equipped with couplers to permit car movement. Cable-operated car pullers are now generally in disfavor because of lack of control of cars being moved. Trailers are often moved by tractors especially equipped with an adjustable "fifth-wheel" coupling, which will couple to any trailer regardless of the height of its coupling.

TRANSPORT OF PACKAGED ITEMS

Vehicle Choice Small units such as **bags, boxes, cartons, carboys, cans, and drums** are usually transported in closed van-type highway vehicles, which may range from small pickup and delivery vehicles of 1400-kg (3000-lb) capacity to trailers capable of holding 23,600 kg (52,000 lb). There has been a trend to higher and wider vehicles, but loading and unloading facilities should be designed to handle not only the newest and largest vehicles but also the older, smaller versions. Figure 21-60*b* shows a typical trailer with principal dimensions.

Ship containers are now predominant for ocean transport of freight in specially designed containerships. They fall into three categories: package-freight containers, tank containers for liquids, and open containers for handling unwieldy items of large size, such as chemical-processing machinery, which are mounted on wood skids. The dominant container sizes are the 20, 40, and 35 foot length. Table 21-29 gives the principal inside dimensions for a variety of package-freight-type containers.

The use of closed railroad cars has declined somewhat in the handling of packaged chemical products in favor of trailers hauled pig-

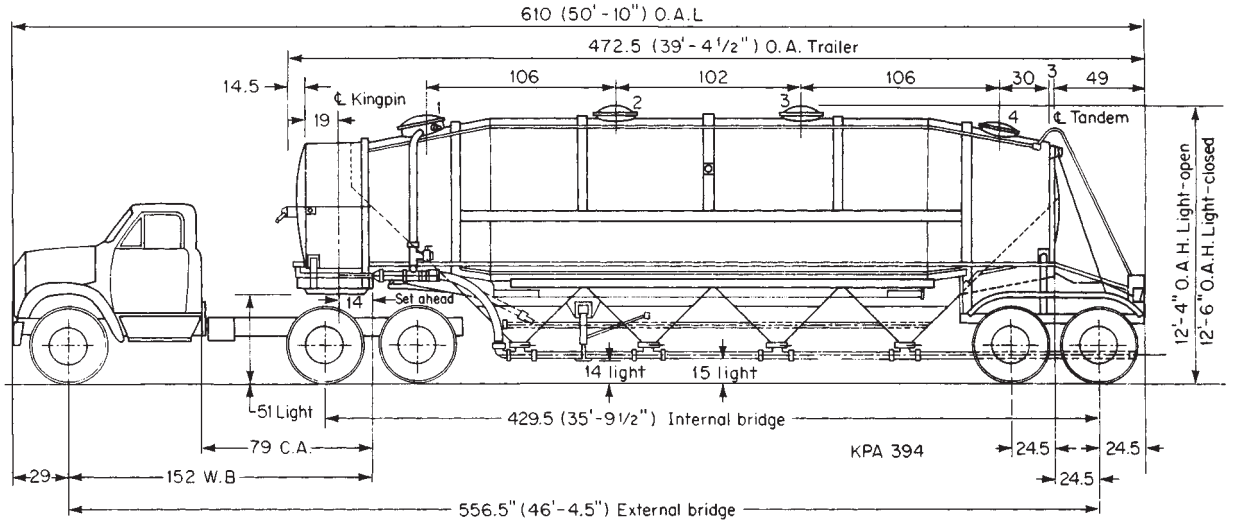


FIG. 21-60*a* Bulk hopper truck. Tractor trailer used for plastics. (*Butler Mfg. Co.*). To convert data to the SI system, change the dimensions shown to inches and multiply by 25.4. To convert volume to cubic meters, multiply cubic feet by 0.02832.

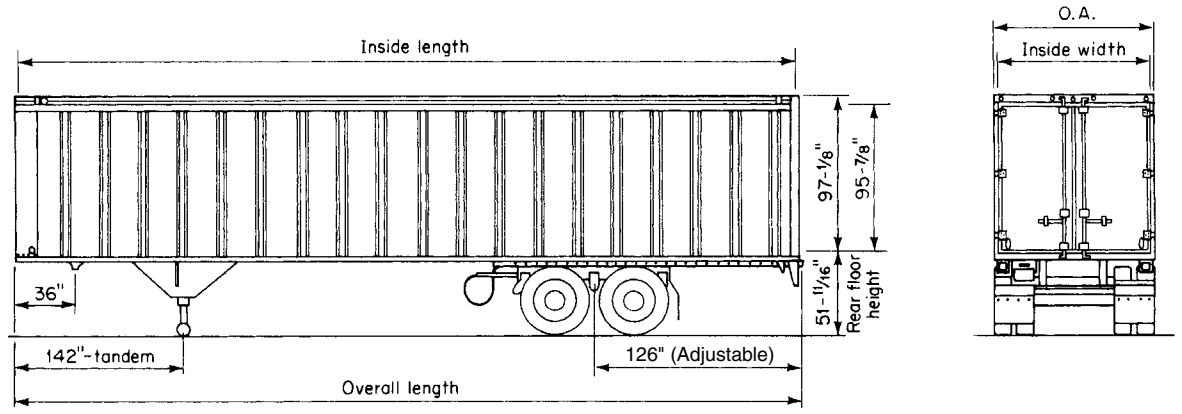


FIG. 21-60*b* Typical inside dimensions for trailers used in North America. Dimensions shown are for an inside height of 96 in. (2438 mm).

gyback fashion by the railroads. This trailer-on-flatcar approach combines the convenience and flexibility of trucks with the low cost and high speed offered by the railroads. Covered railroad cars for hauling packaged freight include not only standard boxcars but much special equipment offering heating, insulation, refrigeration, high volume for low-density products, and special protection for fragile items. Table 21-28 shows principal dimensions for some of this equipment. Of special note is the so-called damage-free (DF) equipment that provides bulkheads with the car. These form modules within the car to keep the freight from shifting during car movement, thus reducing damage.

Pallets These portable platforms, on which packaged materials can be handled and stored (Fig. 21-61 shows several designs), can be had in a variety of standard sizes and in almost any custom-made size. The dimensions, however, tend to be set by the transportation vehicle in which they will move. The older and most common 2235-mm (88-in) truck width and the 2743-mm (108-in) boxcar width have resulted in a "standard" pallet size of 1065 by 1220 mm (42 by 48 in), which fits two across in a truck (the 1065-mm side) and two across in a boxcar (the 1220-mm side), with adequate clearance for maneuvering the lift truck handling them.

There are several variations of this basic size, including the well-used Grocery Manufacturers of America size of 1220 by 1015 mm (48 by 40 in). The choice of the exact size depends on the truck and boxcar width normally available, the size of the package load, and the customer's receiving and handling facilities. Ideally, the sum of the

TABLE 21-29 Typical-Ship-Container Data*

	Length		Width		Height		Volume		Capacity			
									Maximum load†		Tare weight	
Type	ft	mm	ft	mm	ft	mm	ft^3	m^3	lb	kg	lb	kg
20-ft standard‡												
Out	20	6,096	8	2438	8	2438	1,123	31.8	52,913	24,000	4410	2000
In	19.479	5,935	7.771	2370	7.406	2258						
20-ft high§												
Out	20	6,096	8	2438	8.5	2591	1,197	33.9	52,913	24,000	4585	2080
In	19.479	5,935	7.771	2370	7.813	2383						
40-ft standard												
Out	40	12,192	8	2438	8.5	2591	2,430	68.8	59,500	26,990	7700	3490
In	39.594	12,069	7.781	2373	7.896	2405						
40-ft high												
Out	40	12,192	8	2438	9.5	2895	2,684	76.0	60,400	27,400	6800	3080
In	39.563	12,059	7.688	2344	8.823	2689						

*From Hapag Lloyd.

†This is the maximum load that the container will safely carry. The actual load will usually be less because of road weight limits, which vary from country to country and among states and other political subdivisions. In planning, these limits need to be determined with governmental authorities.

‡Liquid tank containers having these outside dimensions and holding 5055 U.S. gal (19,140 L) are available.

§This type of container is also available for dry bulk cargo.

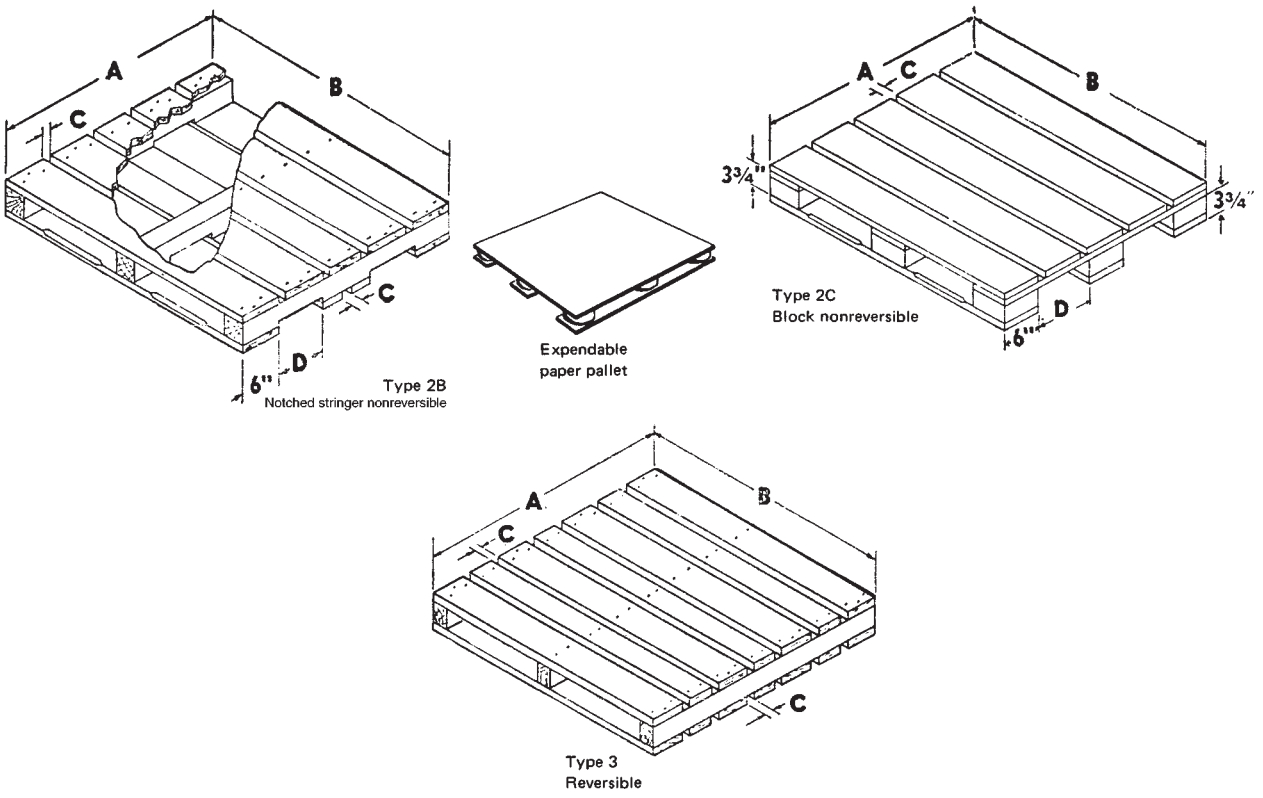


FIG. 21-61 Types of pallets. Designations are standard designs based on nomenclature of the National Wooden Pallet and Container Association, Washington, D.C. Types 2B and 2C are used for bags and corrugated cartons. Type 3 is used for drums and pails.

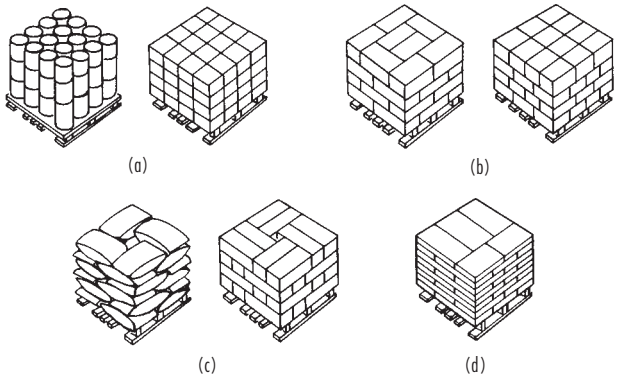


FIG. 21-62 Typical pallet patterns. (*a*) Block pattern is commonly used, although it is often unstable. It may be made more secure by encircling the top tier of containers with wire or strapping. (*b*) Brick pattern is the most commonly used. Containers are interlocked to make a relatively stable load by placing alternate tiers at a 90° position to each other. (*c*) Pinwheel pattern is used when the brick pattern is found to be unstable. Alternate tiers can be interlocked. (*d*) Three-to-two interlocking pattern is used extensively for bagged products. All pallet loads benefit from load-securing systems such as stretch wrap, shrink wrap, or palletizing adhesive.

package dimensions should exactly fit the pallet, but in practice this is virtually impossible. The following rules of thumb are helpful:

For bags: exact pallet dimensions, or up to 13-mm (½-in) overhang on each side

For cartons: pallet dimensions or underhang by 13 mm on each dimension

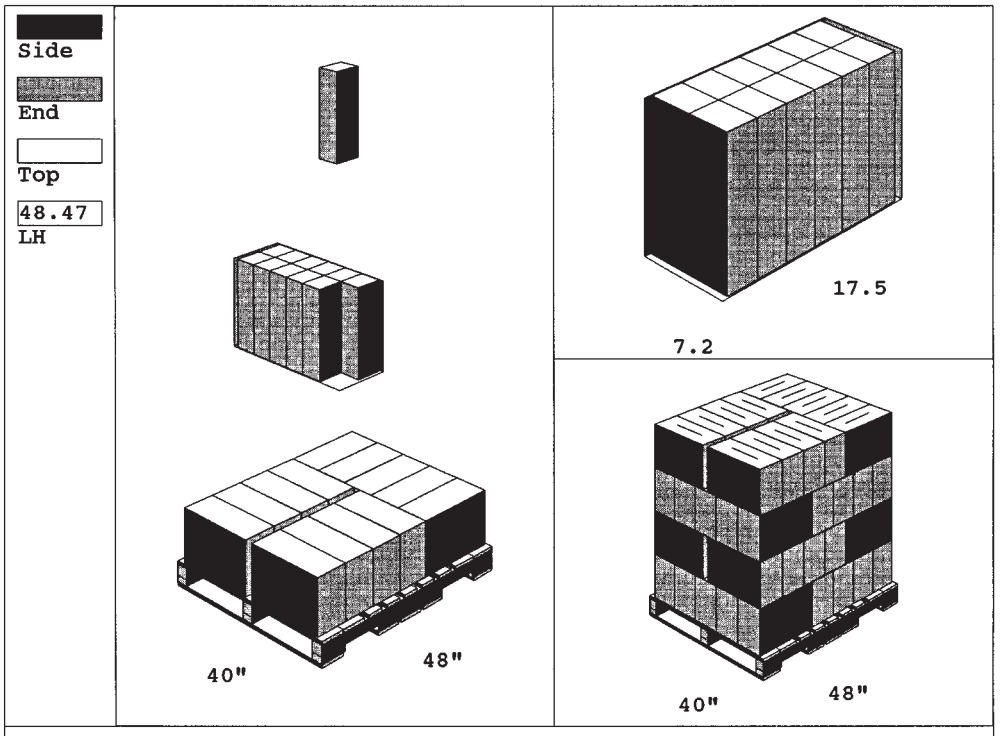
For drums, cylinders, etc.: pallet dimensions or underhang by as much as 25 mm (1 in)

Pallet patterns to achieve these conditions are numerous. Figure 21-62 shows common patterns used in the chemical-process industries.

The traditional material for pallet construction has been hardwood such as oak, ash, and maple. Yellow pine is also often used. Nails and adhesives are used to join component pieces.

The growing shortage of hardwood has increased the cost of wooden pallets to a point at which plastic pallets and composites of wood, paper, and plastics are economically feasible. Much development work is being done on plastic-pallet design to handle typical loadings. Because of the cost of disposing of expendable pallets, returnable ones are often justified.

Blocking and Bracing of Packaged Loads All transportation vehicles impart significant forces to the packages they contain. Forces of up to 2 G are regularly encountered in rail and ocean shipments, and of up to 1 G in trucks. Some forces are caused by vibration of the vehicle in the vertical plane; vibration frequencies are in the 20- to 40-Hz range. Longitudinal forces caused by starting or braking are of similar magnitude under normal conditions, but



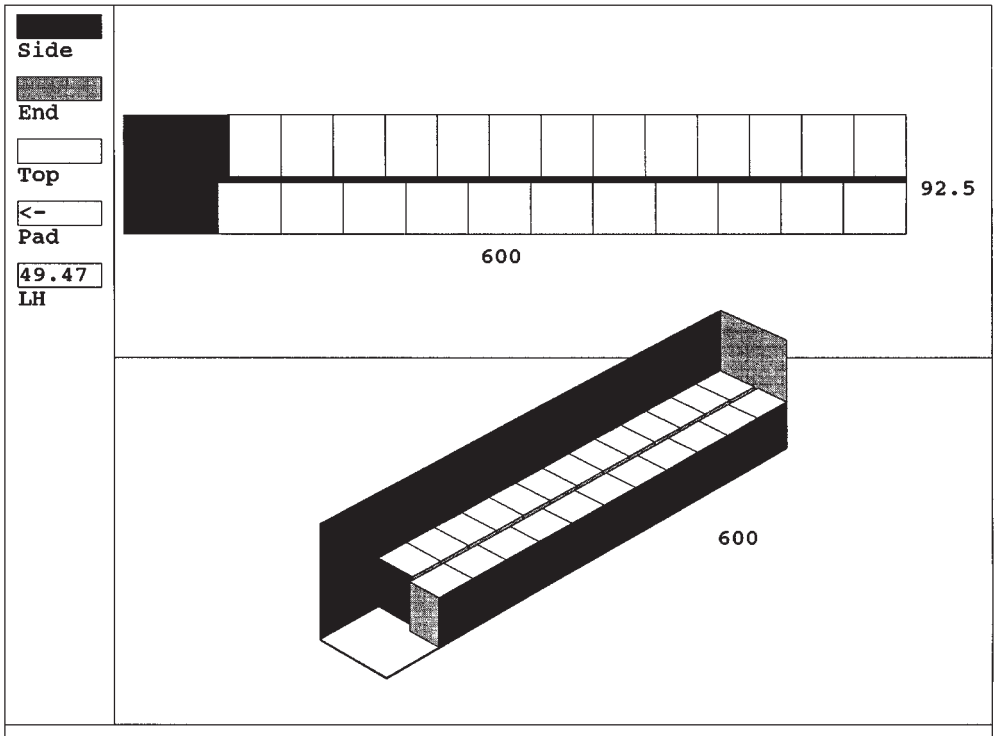
Product Name	Laundry Detergent, SPGR=1						
Product Code	LD						
Datafile Name	RUTGERS (04-04-96)			12	Bottle / Case		
Solution Ref.	1 I			624	Bottle / Load		
Volume Used	80.2 %			13	Case / Tier		
Area Used	88.5 %			4	Tier / Load		
Pallet type	48X40B			52	Case / Load		

	Outside Dimension				Weight			
	Length	Width	Height		Net	Gross		Cube
Bottle	3.500	2.750	10.500	in	2.500	2.800	lb	0.06 cuft
Case	17.675	7.395	10.900	in	33.600	34.357	lb	0.82 cuft
Load	47.255	36.975	48.475	in	1747.200	1851.585	lb	53.86 cuft

FIG. 21-63*a* Use of CAPE software system for determining carton, shipping case, and pallet load dimensions and patterns for defined conditions. Shipping cases must fit within the pallet dimensions. (*Courtesy of CAPE Systems, Inc., Plano, TX, 800-229-3434.*)

severe coupling action or the starting of a long train, through slack action, can cause these forces to reach 6 to 8 G. To protect packaged freight from damage restraining systems have been developed. There are **energy-absorbing blocking and bracing systems** which can absorb these forces with little damage to the packages. Readily available at low cost, these systems are economically justified by reducing or eliminating repackaging cost and by lowering product loss due to package failure. This subject is treated in detail by J. J. Dempsey in *Methods for Loading, Bracing and Blocking of Packaged Goods in Transportation Equipment* (E. I. du Pont de Nemours & Co., Applied Technology Division, Wilmington, DE 19898), which may be purchased from Du Pont at nominal cost. **Simulation of transportation systems** on a laboratory scale is used to predict the effectiveness of freight-restraining systems before actual tryout. The effect of a system on controlling damage at various levels of impact and vibration can be determined quickly and at low cost. As a result, the risk of substantial product loss during initial trials of a new system is reduced significantly. This service is offered by several firms and by the Center for Packaging Science and Engineering, Shock and Vibration Laboratory, Rutgers, The State University of New Jersey, Piscataway, New Jersey.

Distribution packaging design applies primarily to small packages such as found in the household-chemical industry. The competitive nature of household chemicals sold in supermarkets and by mass merchandisers involves frequent change in the design of the primary package—that which is on the supermarket shelf—with a consequent redesign of the secondary protective package in which the point-of-sale packages are shipped. This further influences pallet pattern and loading. Redesign using manual methods can be time consuming, and finding an optimum package is difficult. The era of the personal computer has changed all this. Software which can be run on most 486 personal computers can rapidly evaluate alternative designs and a near optimum established. The CAPE software mentioned previously provides a real-time ability to not only rapidly design the primary and



Product Name	Laundry Detergent, SPGR=1						
Product Code	LD						
Datafile Name	RUTGERS (04-04-96)						
Solution Ref.	1 C						
Volume Used	35.6 %				24	Case / Tier	
Area Used	83.0 %				1	Tier / Load	
Pallet type	50FTTRCK				24	Case / Load	

	Outside Dimension				Weight			
	Length	Width	Height		Net	Gross		Cube
Case	48.000	40.000	48.475	in	1881.600	1924.014	lb	53.86 cuft
Load	527.912	92.480	49.475	in	45158.4	46177.3	lb	1589.04 cuft

FIG. 21-63*b* Use of CAPE for determining trailer loading for conditions of Fig. 21-63*a*, where the maximum cargo weight cannot exceed 46,800 lbs (21,228 kg). Note: CAPE can also give SI units. For Fig. 21-63*a* and *b*, multiply in × 25.4 for mm; cu ft × .02832 for m^3, and lbs × 0.4538 for kg. (*Courtesy of CAPE Systems, Inc., Plano, TX, 800-229-3434.*)

secondary packages and pallet loading, but also determine truck-loading patterns based on highway and road-limit restrictions. Figures 21-63, *a* and *b*, show the design for a one-liter bottle of laundry detergent whose basic dimensions of width, thickness, and height were determined by the industrial designer responsible for the artistic design of the bottle. The CAPE software rapidly evaluates this and in the example given has the restrictions that there can be no overhang of shipping containers over the pallet edges, and that the number of point-of-sale packages in a shipping container is twelve but it can be in any pattern or combination so long as there are twelve bottles in a shipping container. The highway-load restriction is 46,800 pounds. The operation of the CAPE program including loading it into the PC, setting up the case study given, and obtaining results took less than five minutes.

Alternative Separation Processes

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Herbert A. Pohl, Ph.D., *(deceased), Professor of Physics, Oklahoma State University. (Separation Processes Based Primarily on Action in an Electric Field: Dielectrophoresis)*

Kent Pollock, Ph.D., *Member of Technical Staff, Group 91, Space Surveillance Techniques, MIT Lincoln Laboratory. (Separation Processes Based Primarily on Action in an Electric Field: Dielectrophoresis)*

Michael P. Thien, Sc.D., *Senior Research Fellow, Merck & Company, Inc.; Member, American Institute of Chemical Engineers, American Chemical Society, International Society for Pharmaceutical Engineering. (Selection of Biochemical Separation Processes)*

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CRYSTALLIZATION FROM THE MELT

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INTRODUCTION

Purification of a chemical species by solidification from a liquid mixture can be termed either **solution** crystallization or crystallization from the **melt.** The distinction between these two operations is somewhat subtle. The term **melt crystallization** has been defined as the separation of components of a binary mixture without addition of solvent, but this definition is somewhat restrictive. In **solution crystallization** a diluent solvent is added to the mixture; the solution is then directly or indirectly cooled, and/or solvent is evaporated to effect crystallization. The solid phase is formed and maintained somewhat below its pure-component freezing-point temperature. In melt crystallization no diluent solvent is added to the reaction mixture, and the solid phase is formed by cooling of the melt. Product is frequently maintained near or above its pure-component freezing point in the refining section of the apparatus.

A large number of techniques are available for carrying out crystallization from the melt. An abbreviated list includes partial freezing and solids recovery in cooling crystallizer-centrifuge systems, partial melting (e.g., sweating), staircase freezing, normal freezing, zone melting, and column crystallization. A description of all these methods is not within the scope of this discussion. Zief and Wilcox (op. cit.) and Myerson (op. cit.) describe many of these processes. Three of the more common methods—progressive freezing from a falling film, zone melting, and melt crystallization from the bulk—are discussed here to illustrate the techniques used for practicing crystallization from the melt.

High or ultrahigh product purity is obtained with many of the melt-purification processes. Table 22-1 compares the product quality and product form that are produced from several of these operations. Zone refining can produce very pure material when operated in a batch mode; however, other melt crystallization techniques also provide high purity and become attractive if continuous high-capacity processing is desired. Comparison of the features of melt crystallization and distillation are shown on Table 22-2.

A brief discussion of solid-liquid phase equilibrium is presented prior to discussing specific crystallization methods. Figures 22-1 and 22-2 illustrate the phase diagrams for binary solid-solution and eutectic systems respectively. In the case of binary solid-solution systems, illustrated in Fig. 22-1, the liquid and solid phases contain equilibrium quantities of both components in a manner similar to vapor-liquid phase behavior. This type of behavior causes separation difficulties since multiple stages are required. In principle, however, high purity and yields of both components can be achieved since no eutectic is present.

If the impurity or minor component is completely or partially soluble in the solid phase of the component being purified, it is convenient to define a distribution coefficient k, defined by Eq. (22-1):

$$k = C_s/C_\ell \qquad (22\text{-}1)$$

C_s is the concentration of impurity or minor component in the solid phase, and C_ℓ is the impurity concentration in the liquid phase. The distribution coefficient generally varies with composition. The value of k is greater than 1 when the solute raises the melting point and less than 1 when the melting point is depressed. In the regions near pure A or B the liquidus and solidus lines become linear; i.e., the distribution coefficient becomes constant. This is the basis for the common assumption of constant k in many mathematical treatments of fractional solidification in which ultrapure materials are obtained.

In the case of a simple eutectic system shown in Fig. 22-2, a pure solid phase is obtained by cooling if the composition of the feed mix-

TABLE 22-1 Comparison of Processes Involving Crystallization from the Melt

Processes	Approximate upper melting point, °C	Materials tested	Minimum purity level obtained, ppm, weight	Product form
Progressive freezing	1500	All types	1	Ingot
Zone melting				
Batch	3500	All types	0.01	Ingot
Continuous	500	SiI_4	100	Melt
Melt crystallization				
Continuous	300	Organic	10	Melt
Cyclic	300	Organic	10	Melt

Abbreviated from Zief and Wilcox, *Fractional Solidification,* Marcel Dekker, New York, 1967, p. 7.

TABLE 22-2 Comparison of Features of Melt Crystallization and Distillation

Distillation	Melt crystallization
Phase equilibria	
Both liquid and vapor phases are totally miscible.	Liquid phases are totally miscible; solid phases are not.
Conventional vapor/liquid equilibrium.	Eutectic system.
Neither phase is pure.	Solid phase is pure, except at eutectic point.
Separation factors are moderate and decrease as purity increases.	Partition coefficients are very high (theoretically, they can be infinite).
Ultrahigh purity is difficult to achieve.	Ultrahigh purity is easy to achieve.
No theoretical limit on recovery.	Recovery is limited by eutectic composition.
Mass-transfer kinetics	
High mass-transfer rates in both vapor and liquid phases.	Only moderate mass-transfer rate in liquid phase, zero in solid.
Close approach to equilibrium.	Slow approach to equilibrium; achieved in brief contact time. Included impurities cannot diffuse out of solid.
Adiabatic contact assures phase equilibrium.	Solid phase must be remelted and refrozen to allow phase equilibrium.
Phase separability	
Phase densities differ by a factor of 100–10,000:1.	Phase densities differ by only about 10%.
Viscosity in both phases is low.	Liquid phase viscosity moderate, solid phase rigid.
Phase separation is rapid and complete.	Phase separation is slow; surface-tension effects prevent completion.
Countercurrent contacting is quick and efficient.	Countercurrent contacting is slow and imperfect.

Wynn, *Chem. Eng. Prog.,* **88,** 55 (1992). Reprinted with permission of the American Institute of Chemical Engineers. Copyright © 1992 AIChE. All rights reserved

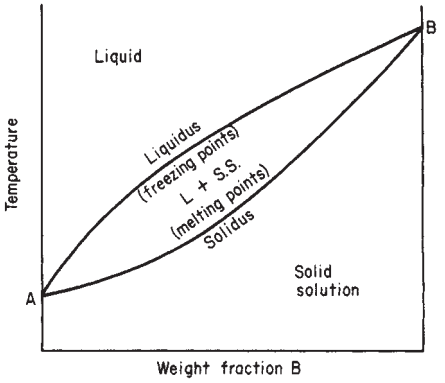


FIG. 22-1 Phase diagram for components exhibiting complete solid solution. (*Zief and Wilcox,* Fractional Solidification, *vol. 1, Marcel Dekker, New York, 1967, p. 31.*)

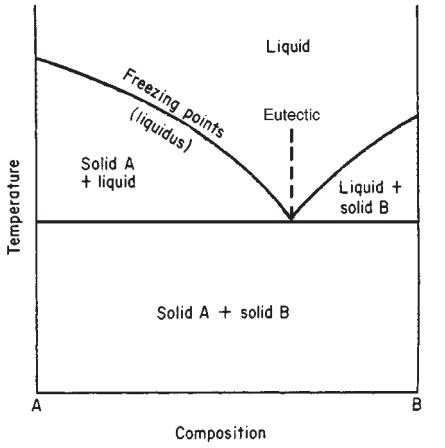


FIG. 22-2 Simple eutectic-phase diagram at constant pressure. (*Zief and Wilcox,* Fractional Solidification, *vol. 1, Marcel Dekker, New York, 1967, p. 24.*)

ture is not at the eutectic composition. If liquid composition is eutectic, then separate crystals of both species will form. In practice it is difficult to attain perfect separation of one component by crystallization of a eutectic mixture. The solid phase will always contain trace amounts of impurity because of incomplete solid-liquid separation, slight solubility of the impurity in the solid phase, or volumetric inclusions. It is difficult to generalize on which of these mechanisms is the major cause of contamination because of analytical difficulties in the ultrahigh-purity range.

The distribution-coefficient concept is commonly applied to fractional solidification of eutectic systems in the ultrapure portion of the phase diagram. If the quantity of impurity entrapped in the solid phase for whatever reason is proportional to that contained in the melt, then assumption of a constant k is valid. It should be noted that the theoretical yield of a component exhibiting binary eutectic behavior is fixed by the feed composition and position of the eutectic. Also, in contrast to the case of a solid solution, only one component can be obtained in a pure form.

There are many types of phase diagrams in addition to the two cases presented here; these are summarized in detail by Zief and Wilcox (op. cit., p. 21). Solid-liquid phase equilibria must be determined experimentally for most binary and multicomponent systems. Predictive methods are based mostly on ideal phase behavior and have limited accuracy near eutectics. A predictive technique based on extracting liquid-phase activity coefficients from *vapor-liquid* equilibria that is useful for estimating nonideal binary or multicomponent *solid-liquid* phase behavior has been reported by Muir (Pap. 71f, 73d ann. meet., AIChE, Chicago, 1980).

PROGRESSIVE FREEZING

Progressive freezing, sometimes called *normal* freezing, is the slow, directional solidification of a melt. Basically, this involves slow solidification at the bottom or sides of a vessel or tube by indirect cooling. The impurity is rejected into the liquid phase by the advancing solid interface. This technique can be employed to concentrate an impurity or, by repeated solidifications and liquid rejections, to produce a very pure ingot. Figure 22-3 illustrates a progressive freezing apparatus. The solidification rate and interface position are controlled by the rate of movement of the tube and the temperature of the cooling medium. There are many variations of the apparatus; e.g., the residual-liquid portion can be agitated and the directional freezing can be carried out vertically as shown in Fig. 22-3 or horizontally (see Richman et al., in Zief and Wilcox, op. cit., p. 259). In general, there is a solute redistribution when a mixture of two or more components is directionally frozen.

Component Separation by Progressive Freezing When the distribution coefficient is less than 1, the first solid which crystallizes contains less solute than the liquid from which it was formed. As the fraction which is frozen increases, the concentration of the impurity in the remaining liquid is increased and hence the concentration of impurity in the solid phase increases (for $k < 1$). The concentration gradient is reversed for $k > 1$. Consequently, in the absence of diffusion in the solid phase a concentration gradient is established in the frozen ingot.

One extreme of progressive freezing is equilibrium freezing. In this case the freezing rate must be slow enough to permit diffusion in the solid phase to eliminate the concentration gradient. When this occurs, there is no separation if the entire tube is solidified. Separation can be achieved, however, by terminating the freezing before all the liquid has been solidified. Equilibrium freezing is rarely achieved in practice because the diffusion rates in the solid phase are usually negligible (Pfann, op. cit., p. 10).

If the bulk-liquid phase is well mixed and no diffusion occurs in the solid phase, a simple expression relating the solid-phase composition to the fraction frozen can be obtained for the case in which the distribution coefficient is independent of composition and fraction frozen [Pfann, *Trans. Am. Inst. Mech. Eng.*, **194,** 747 (1952)].

$$C_s = kC_0(1 - X)^{k-1} \tag{22-2}$$

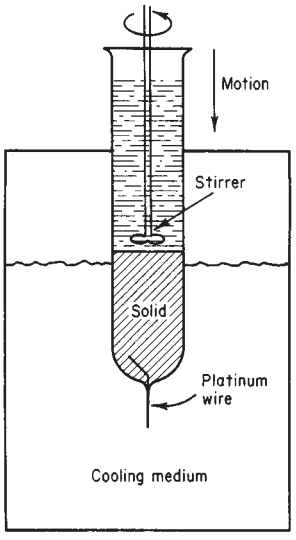


FIG. 22-3 Progressive freezing apparatus.

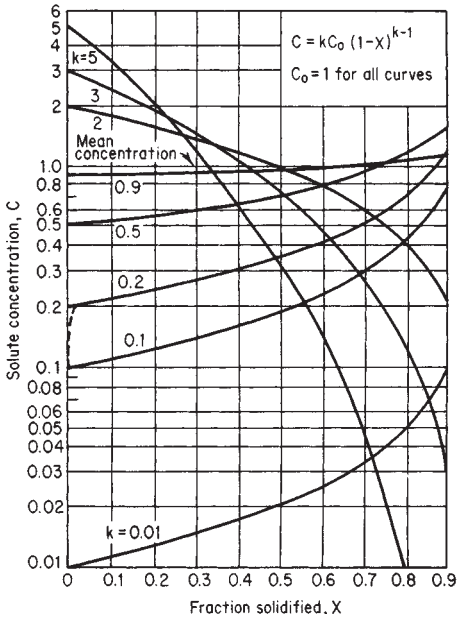


FIG. 22-4 Curves for progressive freezing, showing solute concentration C in the solid versus fraction-solidified X. (*Pfann,* Zone Melting, *2d ed., Wiley, New York, 1966, p. 12.*)

C_0 is the solution concentration of the initial charge, and X is the fraction frozen. Figure 22-4 illustrates the solute redistribution predicted by Eq. (22-2) for various values of the distribution coefficient.

There have been many modifications of this idealized model to account for variables such as the freezing rate and the degree of mixing in the liquid phase. For example, Burton et al. [*J. Chem. Phys.*, **21,** 1987 (1953)] reasoned that the solid rejects solute faster than it can diffuse into the bulk liquid. They proposed that the effect of the freezing rate and stirring could be explained by the diffusion of solute through a stagnant film next to the solid interface. Their theory resulted in an expression for an effective distribution coefficient k_{eff} which could be used in Eq. (22-2) instead of k.

$$k_{\text{eff}} = \frac{1}{1 + (1/k - 1)e^{-f\delta/D}} \tag{22-3}$$

where f = crystal growth rate, cm/s; δ = stagnant film thickness, cm; and D = diffusivity, cm^2/s. No further attempt is made here to summarize the various refinements of Eq. (22-2). Zief and Wilcox (op. cit., p. 69) have summarized several of these models.

Pertinent Variables in Progressive Freezing The dominant variables which affect solute redistribution are the degree of mixing in the liquid phase and the rate of solidification. It is important to attain sufficient mixing to facilitate diffusion of the solute away from the solid-liquid interface to the bulk liquid. The film thickness δ decreases as the level of agitation increases. Cases have been reported in which essentially no separation occurred when the liquid was not stirred. The freezing rate which is controlled largely by the lowering rate of the tube (see Fig. 22-3) has a pronounced effect on the separation achieved. The separation is diminished as the freezing rate is increased. Also fluctuations in the freezing rate caused by mechanical vibrations and variations in the temperature of the cooling medium can decrease the separation.

Applications Progressive freezing has been applied to both solid solution and eutectic systems. As Fig. 22-4 illustrates, large separation factors can be attained when the distribution coefficient is favorable. Relatively pure materials can be obtained by removing the desired portion of the ingot. Also in some cases progressive freezing provides a convenient method of concentrating the impurities; e.g., in the case of $k < 1$ the last portion of the liquid that is frozen is enriched in the distributing solute.

Progressive freezing has been applied on the commercial scale. For example, aluminum has been purified by continuous progressive freezing [Dewey, *J. Metals,* **17,** 940 (1965)]. The Proabd refiner described by Molinari (Zief and Wilcox, op. cit., p. 393) is also a commercial example of progressive freezing. In this apparatus the mixture is directionally solidified on cooling tubes. Purification is achieved because the impure fraction melts first; this process is called sweating. This technique has been applied to the purification of naphthalene and *p*-dichlorobenzene and commercial equipment is available from BEFS PROKEM, Houston, Tx.

ZONE MELTING

Zone melting also relies on the distribution of solute between the liquid and solid phases to effect a separation. In this case, however, one or more liquid zones are passed through the ingot. This extremely versatile technique, which was invented by W. G. Pfann, has been used to purify hundreds of materials. Zone melting in its simplest form is illustrated in Fig. 22-5. A molten zone can be passed through an ingot from one end to the other by either a moving heater or by slowly drawing the material to be purified through a stationary heating zone.

Progressive freezing can be viewed as a special case of zone melting. If the zone length were equal to the ingot length and if only one pass were used, the operation would become progressive freezing. In general, however, when the zone length is only a fraction of the ingot length, zone melting possesses the advantage that a portion of the ingot does not have to be discarded after each solidification. The last portion of the ingot which is frozen in progressive freezing must be discarded before a second freezing.

Component Separation by Zone Melting The degree of solute redistribution achieved by zone melting is determined by the zone length l, ingot length L, number of passes n, the degree of mixing in the liquid zone, and the distribution coefficient of the materials being purified. The distribution of solute after one pass can be obtained by material-balance considerations. This is a two-domain problem; i.e., in the major portion of the ingot of length $L - l$ zone melting occurs in the conventional sense. The trailing end of the ingot of length l undergoes progressive freezing. For the case of constant-distribution coefficient, perfect mixing in the liquid phase, and negligible diffusion in the solid phase, the solute distribution for a single pass is given by Eq. (22-4) [Pfann, *Trans. Am. Inst. Mech. Eng.,* **194,** 747 (1952)].

$$C_s = C_0[1 - (1 - k)e^{-kx/\ell}] \tag{22-4}$$

The position of the zone x is measured from the leading edge of the ingot. The distribution for multiple passes can also be calculated from a material balance, but in this case the leading edge of the zone encounters solid corresponding to the composition at the point in question for the previous pass. The multiple-pass distribution has been numerically calculated (Pfann, *Zone Melting,* 2d ed., Wiley, New York, 1966, p. 285) for many combinations of k, L/l, and n. Typical solute-composition profiles are shown in Fig. 22-6 for various numbers of passes.

The ultimate distribution after an infinite number of passes is also shown in Fig. 22-6 and can be calculated for $x < (L - l)$ from the following equation (Pfann, op. cit., p. 42):

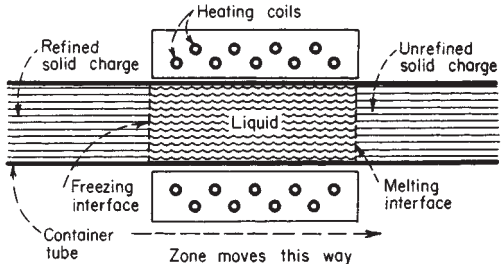


FIG. 22-5 Diagram of zone refining.

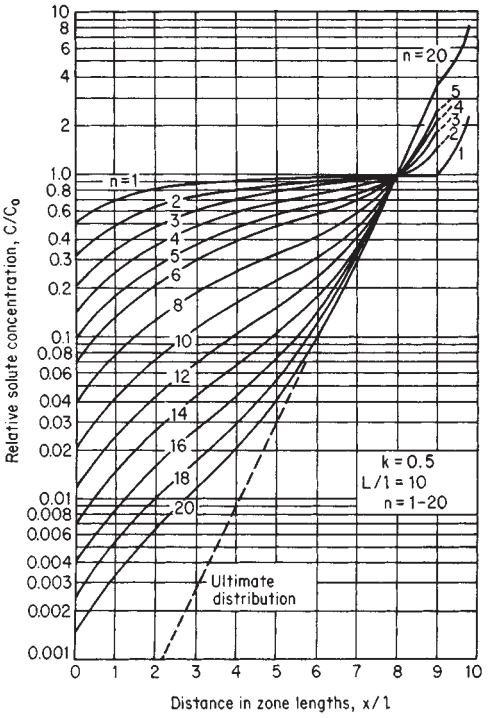


FIG. 22-6 Relative solute concentration C/C_o (logarithmic scale) versus distance in zone lengths x/ℓ from beginning of charge, for various numbers of passes *n*. *L* denotes charge length. (*Pfann,* Zone Melting, *2d ed., Wiley, New York, 1966, p. 290.*)

$$C_s = Ae^{BX} \tag{22-5}$$

where *A* and *B* can be determined from the following relations:

$$k = B\ell/(e^{B\ell} - 1) \tag{22-6}$$

$$A = C_0BL/(e^{BL} - 1) \tag{22-7}$$

The ultimate distribution represents the maximum separation that can be attained without cropping the ingot. Equation (22-5) is approximate because it does not include the effect of progressive freezing in the last zone length.

As in progressive freezing, many refinements of these models have been developed. Corrections for partial liquid mixing and a variable distribution coefficient have been summarized in detail (Zief and Wilcox, op. cit., p. 47).

Pertinent Variables in Zone Melting The dominant variables in zone melting are the number of passes, ingot-length–zone-length ratio, freezing rate, and degree of mixing in the liquid phase. Figure 22-6 illustrates the increased solute redistribution that occurs as the number of passes increases. Ingot-length–zone-length ratios of 4 to 10 are commonly used (Zief and Wilcox, op. cit., p. 624). An exception is encountered when one pass is used. In this case the zone length should be equal to the ingot length; i.e., progressive freezing provides the maximum separation when only one pass is used.

The freezing rate and degree of mixing have effects in solute redistribution similar to those discussed for progressive freezing. Zone travel rates of 1 cm/h for organic systems, 2.5 cm/h for metals, and 20 cm/h for semiconductors are common. In addition to the zone-travel rate the heating conditions affect the freezing rate. A detailed summary of heating and cooling methods for zone melting has been outlined by Zief and Wilcox (op. cit., p. 192). Direct mixing of the liquid region is more difficult for zone melting than progressive freezing. Mechanical stirring complicates the apparatus and increases the probability of contamination from an outside source. Some mixing occurs because of natural convection. Methods have been developed to stir the zone magnetically by utilizing the interaction of a current and magnetic field (Pfann, op. cit., p. 104) for cases in which the charge material is a reasonably good conductor.

Applications Zone melting has been used to purify hundreds of inorganic and organic materials. Many classes of inorganic compounds including semiconductors, intermetallic compounds, ionic salts, and oxides have been purified by zone melting. Organic materials of many types have been zone-melted. Zief and Wilcox (op. cit., p. 624) have compiled tables which give operating conditions and references for both inorganic and organic materials with melting points ranging from −115°C to over 3000°C.

Some materials are so reactive that they cannot be zone-melted to a high degree of purity in a container. Floating-zone techniques in which the molten zone is held in place by its own surface tension have been developed by Keck et al. [*Phys. Rev.,* **89,** 1297 (1953)].

Continuous-zone-melting apparatus has been described by Pfann (op. cit., p. 171). This technique offers the advantage of a close approach to the ultimate distribution, which is usually impractical for batch operation.

Performance data have been reported by Kennedy et al. (*The Purification of Inorganic and Organic Materials,* Marcel Dekker, New York, 1969, p. 261) for continuous-zone refining of benzoic acid.

MELT CRYSTALLIZATION FROM THE BULK

Conducting crystallization inside a vertical or horizontal column with a countercurrent flow of crystals and liquid can produce a higher product purity than conventional crystallization or distillation. The working concept is to form a crystal phase from the bulk liquid, either internally or externally, and then transport the solids through a countercurrent stream of enriched reflux liquid obtained from melted product. The problem in practicing this technology is the difficulty of controlling solid-phase movement. Unlike distillation, which exploits the specific-gravity differences between liquid and vapor phases, melt crystallization involves the contacting of liquid and solid phases that have nearly identical physical properties. Phase densities are frequently very close, and gravitational settling of the solid phase may be slow and ineffective. The challenge of designing equipment to accomplish crystallization in a column has resulted in a myriad of configurations to achieve reliable solid-phase movement, high product yield and purity, and efficient heat addition and removal.

Investigations Crystallization conducted inside a column is categorized as either **end-fed** or **center-fed** depending on whether the feed location is upstream or downstream of the crystal forming section. Figure 22-7 depicts the features of an end-fed commercial column described by McKay et al. [*Chem. Eng. Prog. Symp. Ser.,* no. 25, 55, 163 (1969)] for the separation of xylenes. Crystals of *p*-xylene are formed by indirect cooling of the melt in scraped-surface heat exchangers, and the resultant slurry is introduced into the column at

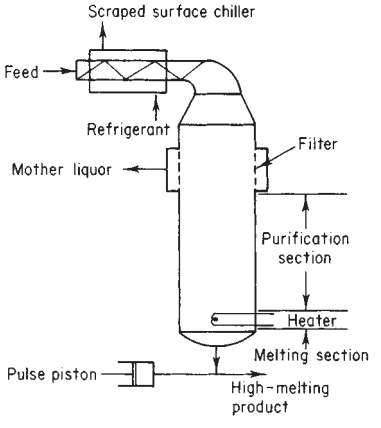


FIG. 22-7 End-fed column crystallizer. (*Phillips Petroleum Co.*)

the top. This type of column has no mechanical internals to transport solids and instead relies upon an imposed hydraulic gradient to force the solids through the column into the melting zone. Residue liquid is removed through a filter directly above the melter. A pulse piston in the product discharge improves washing efficiency and column reliability.

Figure 22-8 shows the features of a horizontal center-fed column [Brodie, *Aust. Mech. Chem. Eng. Trans.*, **37** (May 1979)] which has been commercialized for continuous purification of naphthalene and *p*-dichlorobenzene. Liquid feed enters the column *between* the hot purifying section and the cold freezing or recovery zone. Crystals are formed internally by indirect cooling of the melt through the walls of the refining and recovery zones. Residue liquid that has been depleted of product exits from the coldest section of the column. A spiral conveyor controls the transport of solids through the unit.

Another center-fed design that has only been used on a preparative scale is the vertical spiral conveyor column reported by Schildknecht [*Angew. Chem.*, **73,** 612 (1961)]. In this device, a version of which is shown on Fig. 22-9, the dispersed-crystal phase is formed in the freezing section and conveyed downward in a controlled manner by a rotating spiral with or without a vertical oscillation.

Differences have been observed in the performance of end- and center-fed column configurations. Consequently, discussions of center- and end-fed column crystallizers are presented separately. The design and operation of both columns are reviewed by Powers (Zief and Wilcox, op. cit., p. 343). A comparison of these devices is shown on Table 22-3.

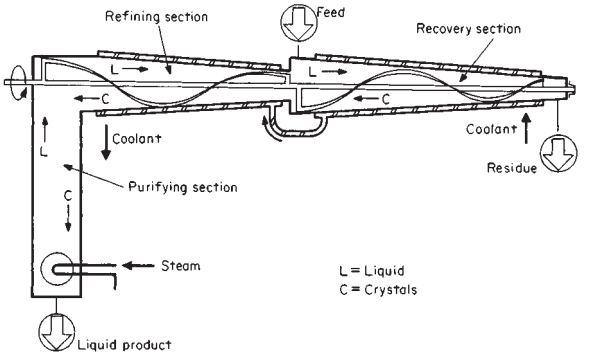


FIG. 22-8 Horizontal center-fed column crystallizer. (*The C. W. Nofsinger Co.*)

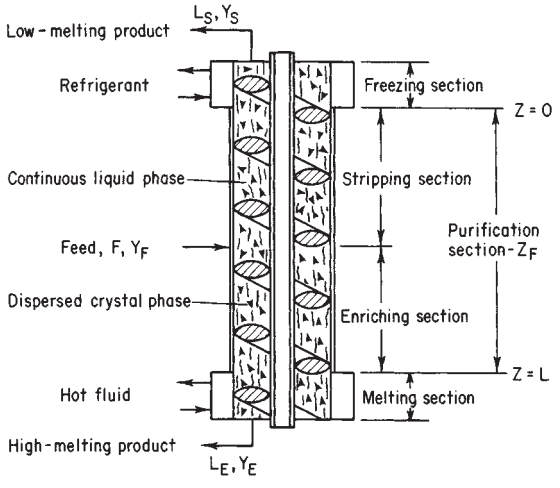


FIG. 22-9 Center-fed column crystallizer with a spiral-type conveyor.

TABLE 22-3 Comparison of Melt-Crystallizer Performance

Center-fed column	End-fed column
Solid phase is formed internally; thus, only liquid streams enter and exit the column.	Solid phase is formed in external equipment and fed as slurry into the purifier.
Internal reflux can be controlled without affecting product yield.	The maximum internal liquid reflux is fixed by the thermodynamic state of the feed relative to the product stream. Excessive reflux will diminish product yield.
Operation can be continuous or batchwise at total reflux.	Total reflux operation is not feasible.
Center-fed columns can be adapted for both eutectic and solid-solution systems.	End-fed columns are inefficient for separation of solid-solution systems.
Either low- or high-porosity-solids-phase concentrations can be formed in the purification and melting zones.	End-fed units are characterized by low-porosity-solids packing in the purification and melting zones.
Scale-up depends on the mechanical complexity of the crystal-transport system and techniques for removing heat. Vertical oscillating spiral columns are likely limited to about 0.2 m in diameter, whereas horizontal columns of several meters are possible.	Scale-up is limited by design of melter and/or crystal-washing section. Vertical or horizontal columns of several meters in diameter are possible.

Center-Fed Column Crystallizers Two types of center-fed column crystallizers are illustrated on Figs. 22-8 and 22-9. As in a simple distillation column, these devices are composed of three distinct sections: a freezing or recovery section, where solute is frozen from the impure liquor; the purification zone, where countercurrent contacting of solids and liquid occurs; and the crystal-melting and -refluxing section. Feed position separates the refining and recovery portions of the purification zone. The section between feed location and melter is referred to as the refining or enrichment section, whereas the section between feed addition and freezing is called the recovery section. The refining section may have provisions for sidewall cooling. The published literature on column crystallizers connotes stripping and refining in a reverse sense to distillation terminology, since refined product from a melt crystallizer exits at the hot section of the column rather than at the cold end as in a distillation column.

Rate processes that describe the purification mechanisms in a column crystallizer are highly complex since phase transition and heat- and mass-transfer processes occur simultaneously. Nucleation and growth of a crystalline solid phase along with crystal washing and crystal melting are occurring in various zones of the apparatus. Column hydrodynamics are also difficult to describe. Liquid- and solid-phase mixing patterns are influenced by factors such as solids-transport mechanism, column orientation, and, particularly for dilute slurries, the settling characteristics of the solids.

Most investigators have focused their attention on a differential segment of the zone between the feed injection and the crystal melter. Analysis of crystal formation and growth in the recovery section has received scant attention. Table 22-4 summarizes the scope of the literature treatment for center-fed columns for both solid-solution and eutectic forming systems.

The dominant mechanism of purification for column crystallization of solid-solution systems is recrystallization. The rate of mass transfer resulting from recrystallization is related to the concentrations of the solid phase and free liquid which are in intimate contact. A model based on height-of-transfer-unit (HTU) concepts representing the composition profile in the purification section for the high-melting component of a binary solid-solution system has been reported by Powers et al. (in Zief and Wilcox, op. cit., p. 363) for total-reflux operation. Typical data for the purification of a solid-solution system, azobenzene-stilbene, are shown in Fig. 22-10. The column crystallizer was operated

TABLE 22-4 Column-Crystallizer Investigations

	Treatments	
	Theoretical	Experimental
Solid solutions		
Total reflux—steady state	1, 2, 4, 6	1, 4, 6
Total reflux—dynamic	2	
Continuous—steady state	1, 4	4, 8, 9
Continuous—dynamic		
Eutectic systems		
Total reflux—steady state	1, 3, 4, 7	1, 3, 6
Total reflux—dynamic		
Continuous—steady state	1, 5, 10, 11, 12	5, 8, 9, 10, 11, 13
Continuous—dynamic		

1. Powers, *Symposium on Zone Melting and Column Crystallization,* Karlsruhe, 1963.
2. Anikin, *Dokl. Akad. Nauk SSSR,* **151,** 1139 (1969).
3. Albertins et al., *Am. Inst. Chem. Eng. J.,* **15,** 554 (1969).
4. Gates et al., *Am. Inst. Chem. Eng. J.,* **16,** 648 (1970).
5. Henry et al., *Am. Inst. Chem. Eng. J.,* **16,** 1055 (1970).
6. Schildknecht et al., *Angew. Chem.,* **73,** 612 (1961).
7. Arkenbout et al., *Sep. Sci.,* **3,** 501 (1968).
8. Betts et al., *Appl. Chem.,* **17,** 180 (1968).
9. McKay et al., *Chem. Eng. Prog. Symp. Ser.,* no. 25, 55, 163 (1959).
10. Bolsaitis, *Chem. Eng. Sci.,* **24,** 1813 (1969).
11. Moyers et al., *Am. Inst. Chem. Eng. J.,* **20,** 1119 (1974).
12. Griffin, M.S. thesis in chemical engineering, University of Delaware, 1975.
13. Brodie, *Aust. Mech. Chem. Eng. Trans.,* 37 (1971).

at total reflux. The solid line through the data was computed by Powers et al. (op. cit., p. 364) by using an experimental HTU value of 3.3 cm.

Most of the analytical treatments of center-fed columns describe the purification mechanism in an adiabatic oscillating spiral column (Fig. 22-9). However, the analyses by Moyers (op. cit.) and Griffin (op. cit.) are for a nonadiabatic dense-bed column. Differential treatment of the horizontal-purifier (Fig. 22-8) performance has not been reported; however, overall material and enthalpy balances have been described by Brodie (op. cit.) and apply equally well to other designs.

A dense-bed center-fed column (Fig. 22-11) having provision for internal crystal formation and variable reflux was tested by Moyers et al. (op. cit.). In the theoretical development (ibid.) a nonadiabatic, plug-flow axial-dispersion model was employed to describe the performance of the entire column. Terms describing interphase transport of impurity between adhering and free liquid are not considered.

A comparison of the axial-dispersion coefficients obtained in oscillating-spiral and dense-bed crystallizers is given in Table 22-5. The dense-bed column approaches axial-dispersion coefficients similar to those of densely packed ice-washing columns.

The concept of minimum reflux as related to column-crystallizer

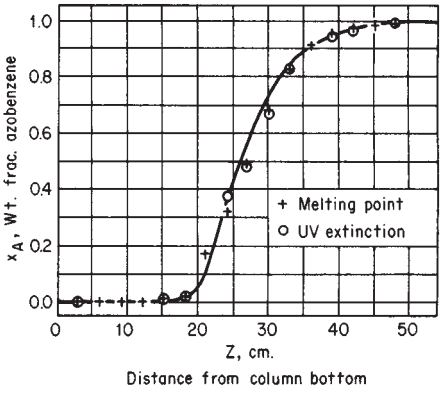


FIG. 22-10 Steady-state separation of azobenzene and stilbene in a center-fed column crystallizer with total-reflux operation. To convert centimeters to inches, multiply by 0.3937. (*Zief and Wilcox,* Fractional Solidification, *vol. 1, Marcel Dekker, New York, 1967, p. 356.*)

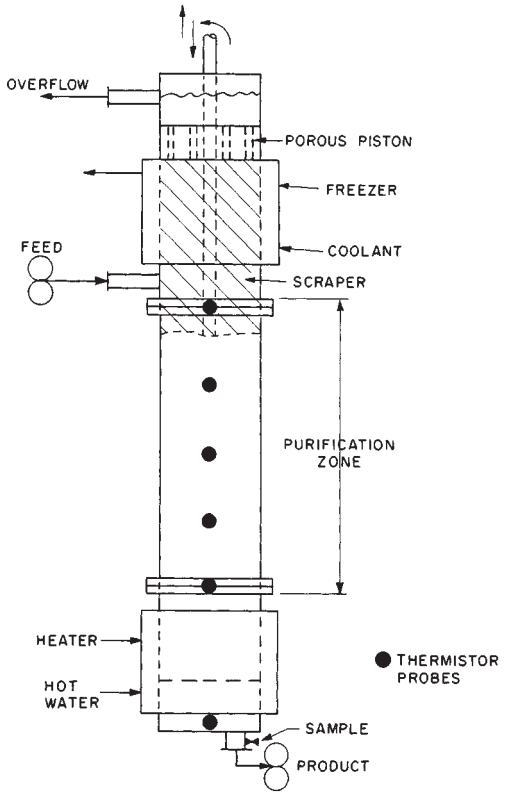


FIG. 22-11 Dense-bed center-fed column crystallizer. [*Moyers et al.,* Am. Inst. Chem. Eng. J., ***20,*** *1121 (1974).*]

operation is presented by Brodie (op. cit.) and is applicable to all types of column crystallizers, including end-fed units. In order to stabilize column operation the sensible heat of subcooled solids entering the melting zone should be balanced or exceeded by the heat of fusion of the refluxed melt. The relationship in Eq. (22-8) describes the minimum reflux requirement for proper column operation.

$$R = (T_P - T_F)\, C_P/\lambda \qquad (22\text{-}8)$$

R = reflux ratio, g reflux/g product; T_P = product temperature, °C; T_F = saturated-feed temperature, °C; C_P = specific heat of solid crystals, cal/(g·°C); and λ = heat of fusion, cal/g.

All refluxed melt will refreeze if reflux supplied equals that computed by Eq. (22-8). When reflux supplied is greater than the minimum, jacket cooling in the refining zone or additional cooling in the recovery zone is required to maintain product recovery. Since high-

TABLE 22-5 Comparison of Axial-Dispersion Coefficients for Several Liquid-Solid Contactors

Column type	Dispersion coefficient, cm^2/s	Reference
Center-fed crystallizer (oscillating spiral)	1.6–3.5	1
Center-fed crystallizer (oscillating spiral)	1.3–1.7	2
Countercurrent ice-washing column	0.025–0.17	3
Center-fed crystallizer	0.12–0.30	4

References:
1. Albertins et al., *Am. Inst. Chem. Eng. J.,* **15,** 554 (1969).
2. Gates et al., *Am. Inst. Chem. Eng. J.,* **16,** 648 (1970).
3. Ritter, Ph.D. thesis, Massachusetts Institute of Technology, 1969.
4. Moyers et al., *Am. Inst. Chem. Eng. J.,* **20,** 1119 (1974).

purity melts are fed near their pure-component freezing temperatures, little refreezing takes place unless jacket cooling is added.

To utilize a column-crystallizer design or rating model, a large number of parameters must be identified. Many of these are empirical in nature and must be determined experimentally in equipment identical to the specific device being evaluated. Hence macroscopic evaluation of systems by large-scale piloting is the rule rather than the exception. Included in this rather long list of critical parameters are factors such as impurity level trapped in the solid phase, product quality as a function of reflux ratio, degree of liquid and solids axial mixing in the equipment as a function of solids-conveyor design, size and shape of crystals produced, and ease of solids handling in the column. Heat is normally removed through metal surfaces; thus, the stability of the solution to subcooling can also be a major factor in design.

End-Fed Column Crystallizer End-fed columns were developed and successfully commercialized by the Phillips Petroleum Company in the 1950s. The sections of a typical end-fed column, often referred to as a Phillips column, are shown on Fig. 22-7. Impure liquor is removed through filters located between the product-freezing zone and the melter rather than at the end of the freezing zone, as occurs in center-fed units. The purification mechanism for end-fed units is basically the same as for center-fed devices. However, there are reflux restrictions in an end-fed column, and a high degree of solids compaction exists near the melter of an end-fed device. It has been observed that the free-liquid composition and the fraction of solids are relatively constant throughout most of the purification section but exhibit a sharp discontinuity near the melting section [McKay et al., *Ind. Eng. Chem.*, **52,** 197 (1969)]. Investigators of end-fed column behavior are listed in Table 22-6. Note that end-fed columns are adaptable only for eutectic-system purification and cannot be operated at total reflux.

Performance information for the purification of *p*-xylene indicates that nearly 100 percent of the crystals in the feed stream are removed as product. This suggests that the liquid which is refluxed from the melting section is effectively refrozen by the countercurrent stream of subcooled crystals. A high-melting product of 99.0 to 99.8 weight percent *p*-xylene has been obtained from a 65 weight percent *p*-xylene feed. The major impurity was *m*-xylene. Figure 22-12 illustrates the column-cross-section-area–capacity relationship for various product purities.

Column crystallizers of the end-fed type can be used for purification of many eutectic-type systems and for aqueous as well as organic systems (McKay, loc. cit.). Column crystallizers have been used for xylene isomer separation, but recently other separation technologies including more efficient melt crystallization equipment have tended to supplant the Phillips style crystallizer.

Commercial Equipment and Applications In the last two decades the practice of melt crystallization techniques for purification of certain organic materials has made significant commercial progress. The concept of refining certain products by countercurrent staging of crystallization in a column has completed the transition from laboratory and pilot equipment to large-scale industrial configurations. Chemicals which have been purified by suspension crystallization-purifier column techniques are listed on Table 22-7. The practice of crystal formation and growth from the bulk liquid (as is practiced in suspension crystallization techniques described in Sec. 18 of this handbook) and subsequent crystal melting and refluxing in a purifier column has evolved into two slightly different concepts: (1) the horizontal continuous crystallization technique with vertical purifier invented by Brodie (op. cit.) and (2) the continuous multistage or stepwise system with vertical purifier developed by Tsukishima Kikai Co., Ltd. (TSK). A recent description of these processes has been published by Meyer [*Chem. Proc.*, **53,** 50 (1990)].

TABLE 22-6 End-Fed-Crystallizer Investigations

Eutectic systems	Treatments	
	Theoretical	Experimental
Continuous—steady state	1, 2, 4	1, 4
Batch	3	3

1. McKay et al., *Ind. Eng. Chem. Process Des. Dev.*, **6,** 16 (1967).
2. Player, *Ind. Eng. Chem. Process Des. Dev.*, **8,** 210 (1969).
3. Yagi et al., *Kagaku Kogaku*, **72,** 415 (1963).
4. Shen and Meyer, Prepr. 19F, AIChE Symp., Chicago, 1970.

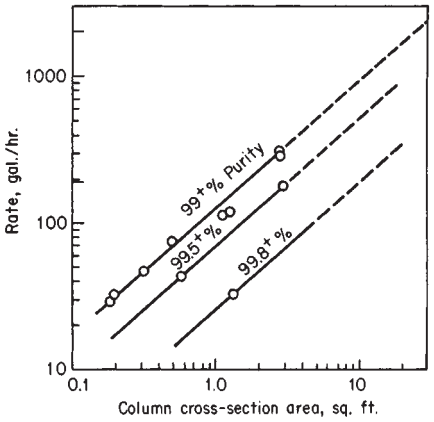


FIG. 22-12 Pulsed-column capacity versus column size for 65 percent *p*-xylene feed. To convert gallons per hour to cubic meters per hour, multiply by 0.9396; to convert square feet to square meters, multiply by 0.0929. (*McKay et al., prepr., 59th nat. meet. AIChE, East Columbus, Ohio.*)

In the multistage process described on Fig. 22-14 feed enters one of several crystallizers installed in series. Crystals formed in each crystallizer are transferred to a hotter stage and the liquid collected in the clarified zone of the crystallizer is transferred to a colder stage and eventually discharged as residue. At the hot end, crystals are transferred to a vertical purifier where countercurrent washing is performed by pure, hot-product reflux. TSK refers to this multistage process as the countercurrent cooling crystallization (CCCC) process. In principle any suitable type of crystallizer can be used in the stages

TABLE 22-7 Chemicals Purified by TSK CCCC Process (The C. W. Nofsinger Co.)

Acetic acid	Isophthaloyl chloride
Acrylic acid	Isopregol
Adipic acid	Lutidine
Benzene	Maleic anhydride
Biphenyl	Naphthalene
Bisphenol-A	*p*-Nitrochloro benzene
Caprolactam	*p*-Nitrotoluene
Chloroacetic acid	Phenol
p-Chloro toluene	*b*-Picoline
p-Cresol	*g*-Picoline
Combat (proprietary)	Pyridine
Dibutyl hydroxy toluene (BHT)	Stilbene
p-Dichloro benzene	Terephthaloyl chloride
2,5 Dichlorophenol	Tertiary butyl phenol
Dicumyl peroxide	Toluene diisocyanate
Diene	Trioxane
Heliotropin	*p*-Xylene
Hexachloro cyclo butene	3,4 Xylidine
Hexamethylene diamine	

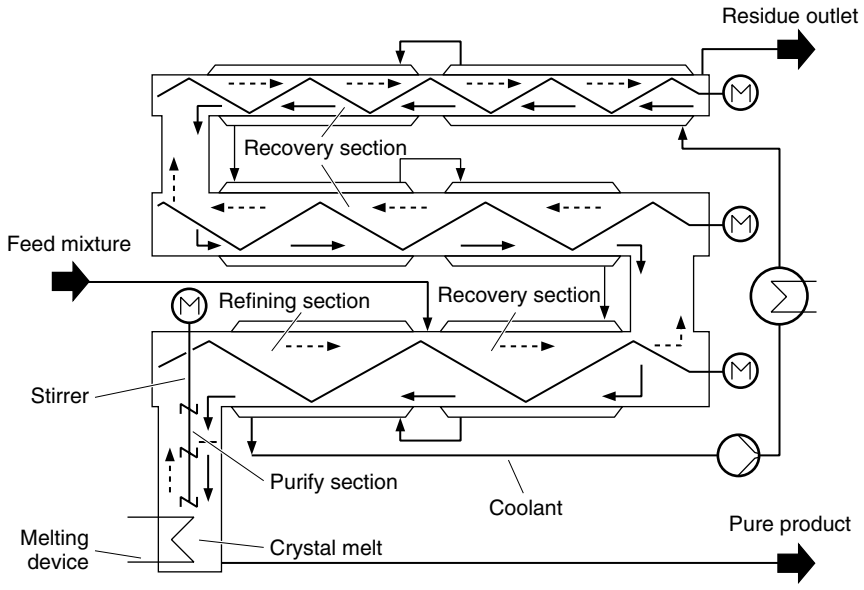


FIG. 22-13 Horizontal continuous Brodie melt crystallizer—multitube unit. (*The C. W. Nofisinger Co.*)

TABLE 22-8 Commercial TSK Crystallization Operating Plants

	Capacity MM lbs/yr	Company	Date & location
Countercurrent Cooling Crystallization (CCCC) Process			
Nofsinger license			
Nofsinger design & construct			
p-Dichlorobenzene	Confidential	Monsanto Co.	1989—Sauget, IL
TSK license			
TSK design & construct			
Confidential[1]	Confidential	Confidential	1988—Japan
p-Xylene	137	MGC	1986—Mizushima, Japan
Confidential[2]	Confidential	Confidential	1985—Japan
p-Xylene	132	MGC	1983—Mizushima, Japan
	expanded to 160		1984—Japan
p-Xylene	26.5	MGC	1981—Mizushima, Japan
Brodie			
TSK license			
TSK design & construct			
Naphthalene	8	SHSM	1985—China
p-DCB	13	Hodogaya	1981—Japan
p-DCB	5.5	Sumitomo	1978—Japan
UCAL license & design			
TSK hardware			
Naphthalene	16	Nippon Steel	1974—Japan
p-DCB	13	Hodogaya	1974—Japan
UCAL license & design			
Naphthalene	10	British Tar	1972—U.K.
p-DCB	3	UCAL	1969—Australia

ABBREVIATIONS:
Nofsinger The C. W. Nofsinger Company
TSK Tsukishima Kikai Co., Ltd.
SHSM Shanghai Hozan Steel Mill
UCAL Union Carbide Australia, Ltd.
MGC Mitsubishi Gas Chemical Co., co-developer with TSK of the application for *p*-Xylene

1. Commercial scale plant started up in the spring of 1988 purifying a bulk chemical. This is the first application of the CCCC process on this bulk chemical.
2. This small unit is operating in Japan with an 800 mm crystallizer and 300 mm purifier. Because of confidentiality, we cannot disclose the company, capacity, or product.

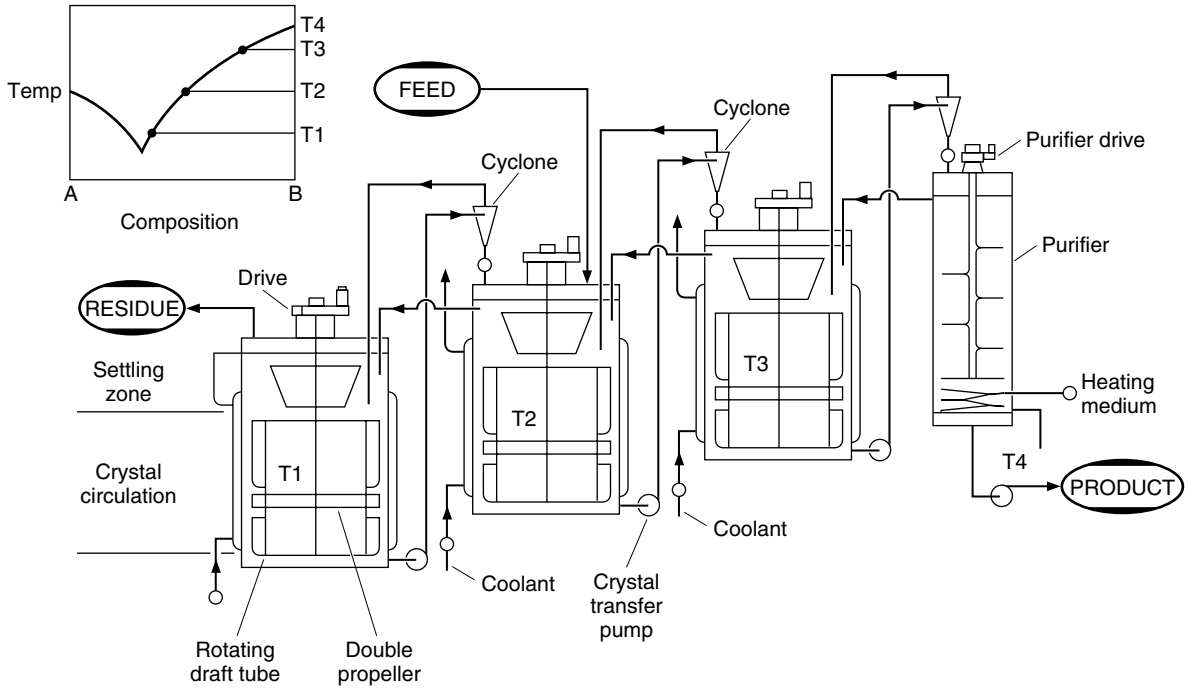


FIG. 22-14 Crystallizer—multistage process. (*The C. W. Nofisinger Co.*)

as long as the crystals formed can be separated from the crystallizer liquid and settled and melted in the purifier.

Commercial applications for both the Brodie and CCCC process are indicated on Table 22-8. Both the Brodie Purifier and the CCCC processes are available from The C. W. Nofsinger Company, PO Box 419173, Kansas City, MO 64141-0173.

FALLING-FILM CRYSTALLIZATION

Falling-film crystallization utilizes progressive freezing principles to purify melts and solutions. The technique established to practice the process is inherently cyclic. Figure 22-15 depicts the basic working concept. First a crystalline layer is formed by subcooling a liquid film

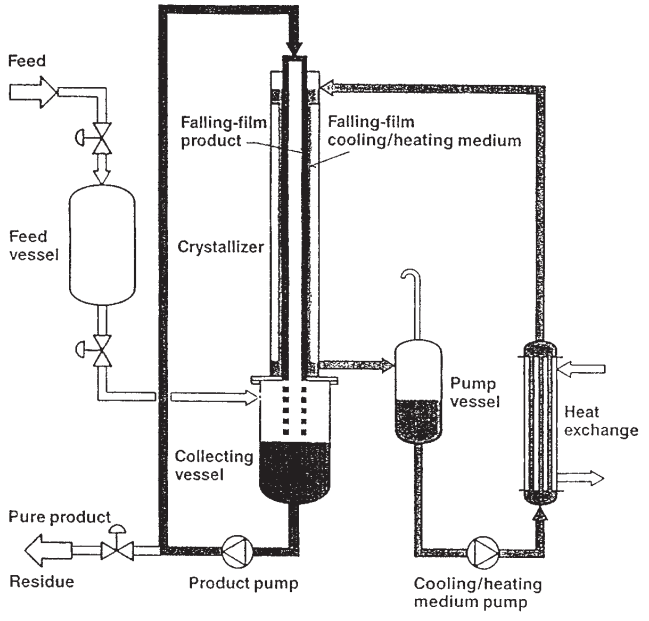
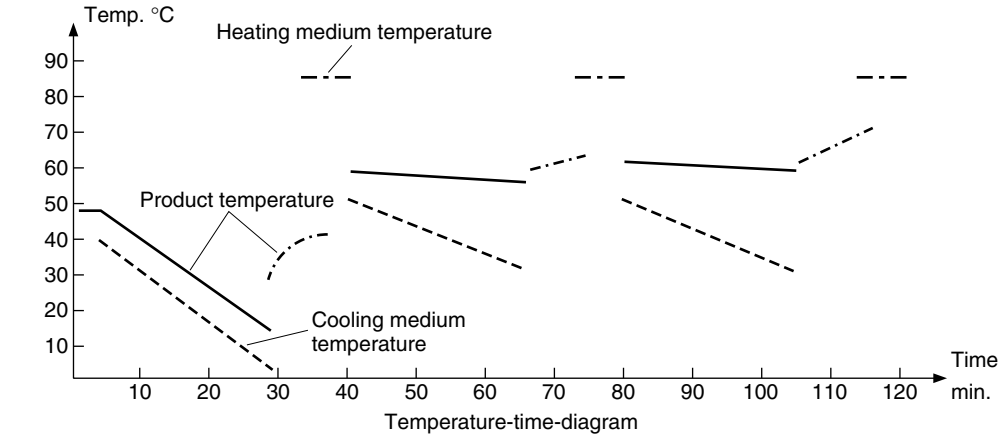
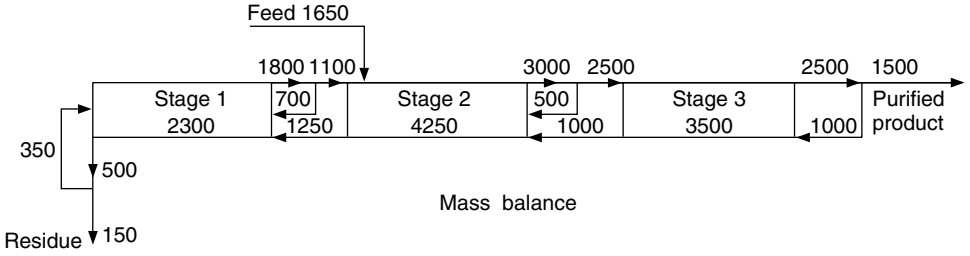


FIG. 22-15 Dynamic crystallization system. (*Sulzer Chemtech*)

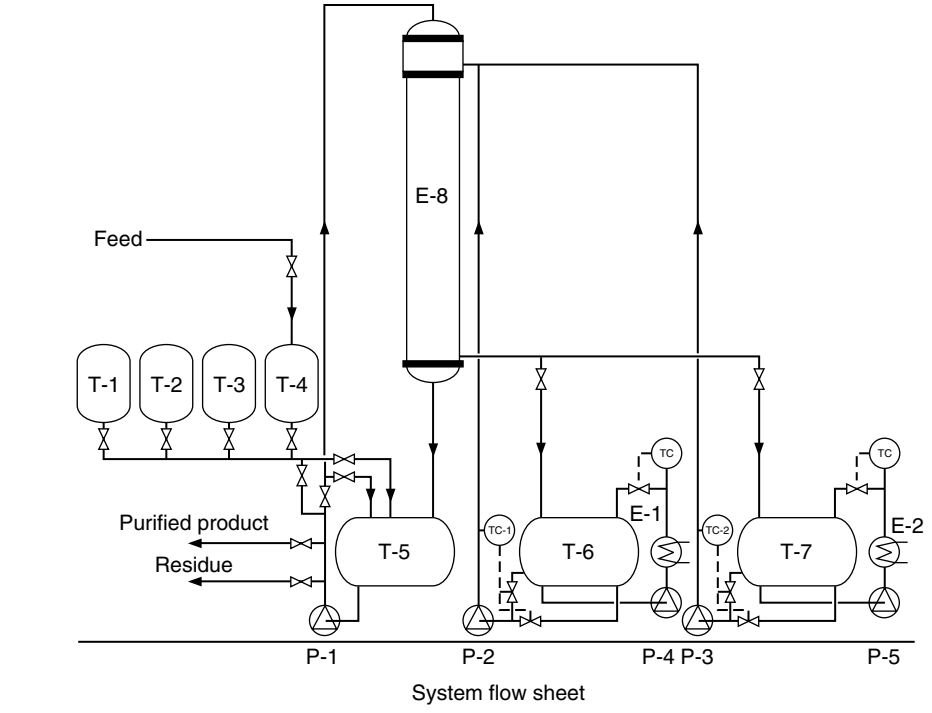


Temperature-time-diagram



Mass balance

(a)



System flow sheet

(b)

FIG. 22-16 Sulzer MWB-crystallization process. (*a*) Stepwise operation of the process. (*b*) System flow sheet. (*Sulzer Chemtech*)

on a vertical surface inside a tube. This coating is then grown by extracting heat from a falling film of melt (or solution) through a heat transfer surface. Impure liquid is then drained from the crystal layer and the product is reclaimed by melting. Variants of this technique have been perfected and are used commercially for many types of organic materials. Both static and falling-film techniques have been described by Wynn [*Chem. Eng. Progr.*, (1992)]. Mathematical models for both static and dynamic operations have been presented by Gilbert [*AIChE J.*, **37,** 1205 (1991)].

Principles of Operation Figure 22-16 describes a typical three-stage falling-film crystallization process for purification of MCA (monochloro acetic acid). Crystallizer E-8 consists of a number of vertical tubular elements working in parallel enclosed in a shell. Normal tube length is 12 meters with a 50- to 75-millimeter tube inside diameter. Feed enters stage two of the sequential operation, is added to the kettle (T-5), and is then circulated to the top of the crystallizer and distributed as a falling film inside the tubes. Nucleation is induced at the inside walls and a crystal layer starts to grow. Temperature of the coolant is progressively lowered to compensate for reduced heat transfer and lower melt freezing point until the thickness inside the tube is between 5 and 20 millimeters depending on the product. Kettle liquid is evactuated to the first-stage holding tank (T-3) for eventual recrystallization at a lower temperature to maximize product yield and to strip product from the final liquid residue. Semirefined product frozen to the inside of the tube during operation of stage two is first heated above its melting point and slightly melted (sweated). This semipurified melted material (sweat) is removed from the crystallizer kettle, stored in a stage tank (T-4), and then added to the next batch of fresh feed. The remaining material inside the crystallizer is then melted, mixed with product sweat from stage three, recrystallized, and sweated to upgrade the purity even further (stage 3).

Commercial Equipment and Applications The falling-film crystallization process was invented by the MWB company in Switzerland. The process is now marketed by Sulzer Chemtech. Products successfully processed in the falling-film crystallizer are listed on Table 22-9. The falling-film crystallization process is available from the Chemtech Div. of Sulzer Canada Inc., 60 Worcester Rd., Rexdale, Ontario N9W 5X2 Canada.

TABLE 22-9 Fractional Crystallization Reference List

Product	Main characteristics	Capacity, tons/year	Purity	Type of plant	Country	Client
Acrylic acid	Very low aldehyde content, no undesired polymerization in the plant	Undisclosed Undisclosed	99.95% 99.9%	Falling film Falling film	Undisclosed Undisclosed	Undisclosed Undisclosed
Benzoic acid	Pharmaceutical grade, odor- and color free	4,500	99.97%	Falling film	Italy	Chimica del Friuli
Bisphenol A	Polycarbonate grade, no solvent required	150,000	Undisclosed	Falling film	USA	General Electric
Carbonic acid		1,200	Undisclosed	Falling film	Germany	Undisclosed
Fatty acid	Separation of tallow fatty acid into saturated and unsaturated fractions	20,000	Stearic acid: Iodine no. 2 Oleic acid: Cloud pt 5°C	Falling film	Japan	Undisclosed
Fine chemicals		<1,000 <1,000 <1,000 <1,000 <1,000 <1,000 <1,000	Undisclosed Undisclosed Undisclosed Undisclosed Undisclosed Undisclosed Undisclosed	Falling film Static Falling film Falling film Falling film Falling film Falling film	GUS Switzerland Switzerland Switzerland USA Germany Japan	Undisclosed Undisclosed Undisclosed Undisclosed Undisclosed Undisclosed Undisclosed
Hydrazine	Satellite grade	3	>99.9%	Falling film	Germany	ESA
Monochloro acetic acid (MCA)	Low DCA content	6,000	>99.2%	Falling film	USA	Undisclosed
Multipurpose	Separation or purification of two or more chemicals, alternatively	1,000 1,000	Various grades Undisclosed	Falling film Falling film	Belgium Belgium	UCB Reibelco
Naphthalene	Color free and color stable with low thionaphthene content	60,000 20,000 10,000 12,000	99.5% 99.5% 99.8% Various grades	Falling film Falling film/static Falling film/static Falling film	Germany P.R. China P.R. China The Netherlands	Rütgers-Werke Anshan Jining Cindu Chemicals
p-Dichlorobenzene	No solvent washing required	40,000 5,000 4,000 3,000 3,000	99.95% 99.98% 99.8% 99.95% >97%	Falling film Falling film Falling film/distillation Falling film Static	USA Japan Brazil P.R. China P.R. China	Standard Chlorine Toa Gosei Nitroclor Fuyang Shandong
p-Nitrochlorobenzene		18,000 10,000	99.3% 99.5%	Falling film/distillation Static	P.R. China India	Jilin Chemical Mardia
Toluene diisocyanate (TDI)	Separation of TDI 80 into TDI 100 & TDI 65	22,000	Undisclosed	Falling film	Undisclosed	Undisclosed
Trioxan		<1,000	99.97%	Falling film	Undisclosed	Undisclosed

SUPERCRITICAL FLUID SEPARATION PROCESSES

General References: Bruno and Ely, *Supercritical Fluid Technology: Reviews in Modern Theory and Applications,* CRC Press, Boca Raton, 1991. Brunner, *Gas Extraction: An Introduction to Fundamentals of Supercritical Fluids and the Application to Separation Processes,* Springer, New York, 1994. Gloyna and Li, *Waste Management,* **13,** 379 (1993). Johnston and Penninger, *Supercritical Fluid Science and Technology,* Am. Chem. Soc. Symp. Series, **406**, 1989. Kiran and Brennecke, *Am. Chem. Soc. Symp. Ser.,* **512**, 1993. Kiran and Sengers, *Supercritical Fluids: Fundamentals for Application;* NATO Adv. Study Inst. Series E, 1994, Kluwer, Boston, 1994, p. 273. McHugh and Krukonis, *Supercritical Fluid Extraction: Principles and Practice, 2d ed.*. Butterworth-Heinemann, Boston, 1994. Paulaitis, Krukonis, Kurnik, and Reid, *Rev. Chem. Eng.*, **1,** 179 (1983). Savage, Gopalan, Mizan, Martino, and Brock, *AIChE J.*, **41,** 1723 (1995). Shaw, Brill, Clifford, Eckert, and Franck, *Chem. Eng. News,* **69,** 26 (1991). Stahl, Quirin, and Gerard, *Dense Gases for Extraction and Refining,* Springer-Verlag, Berlin, 1988. Tester, Holgate, Armellini, Webley, Killilea, Hong, and Barnes, *Am. Chem. Soc. Symp. Ser.,* **518,** 1993, p. 35.

INTRODUCTION

Fluids above their critical temperatures and pressures, called supercritical fluids (SCFs), exhibit properties intermediate between those of gases and liquids. Consequently, each of these two boundary conditions shed insight into the nature of these fluids. Unlike gases, SCFs possess a considerable solvent strength, transport properties are more favorable (e.g., lower viscosities and higher diffusion coefficients, than in liquid solvents). In regions where a SCF is highly compressible, its density and hence its solvent strength may be adjusted over a wide range with modest variations in temperature and pressure. This tunability may be used to control phase behavior, separation processes (e.g., SCF extraction), rates and selectivities of chemical reactions, and morphologies in materials processing. A variety of advantages of SCF separation processes are given in Table 22-10. In some cases these advantages compensate for the disadvantage of the need for elevated pressure. Despite the diversity of SCF separation processes (see Table 22-11), an attempt will be made to identify unifying themes.

TABLE 22-10 Advantages of Supercritical Fluid Separations

Adjustable solvent strength to tailor selectivities and yields.
Higher diffusion coefficients and lower viscosities compared with liquids.
Rapid diffusion of CO_2 through condensed phases, e.g. polymers.
Solvent recovery is fast and complete, with minimal residue in product.
Properties of CO_2 as a solvent:
Environmentally acceptable solvent for waste minimization, nontoxic, nonflammable, inexpensive, usable at mild temperatures.
Properties of water as a solvent:
Nontoxic, nonflammable substitute for organic solvents.
Extremely wide variation in solvent strength with temperature and pressure.
Collapse of structure due to capillary forces is prevented during solvent removal.

TABLE 22-11 Commercial Applications of Supercritical Fluid Separations Technology

Extraction of foods and pharmaceuticals
Coffee and tea decaffeination
Flavors from hops
Cholesterol and fat from eggs
Nicotine from tobacco
Acetone from antibiotics
Extraction of organics from water
Extraction of volatile substances from substrates
Drying and aerogel formation
Cleaning, e.g. quartz rods for light guide fibers
Removal of monomers, oligomers, and solvent from polymers
Fractionation
Residuum oil supercritical extraction-petroleum deasphalting
Polymer fractionation
Edible oils fractionation
Analytical SCF extraction and chromatography
Reactive separations
Extraction of sec-butanol from isobutene
Hydrothermal oxidation of organic wastes in water

The two fluids most often studied in supercritical fluid technology, carbon dioxide and water, are the two least expensive of all solvents. Carbon dioxide is nontoxic, nonflammable, and has a near-ambient critical temperature of 31.1°C. CO_2 is an environmentally friendly substitute for organic solvents including chlorocarbons and chlorofluorocarbons. Supercritical water (T_c = 374°C) is of interest as a substitute for organic solvents to minimize waste in extraction and reaction processes. Additionally, it is used for hydrothermal oxidation of hazardous organic wastes (also called supercritical water oxidation) and hydrothermal synthesis.

PHYSICAL PROPERTIES OF PURE SUPERCRITICAL FLUIDS

Thermodynamic Properties The variation in solvent strength of a supercritical fluid from gaslike to liquidlike values may be described qualitatively in terms of the density, ρ, or the solubility parameter, δ (square root of the cohesive energy density). It is shown for gaseous, liquid, and SCF CO_2 as a function of pressure in Fig. 22-17 according to the rigorous thermodynamic definition:

$$\delta = \left(\frac{u^{ig} - u}{v}\right)^{1/2} = \left(\frac{h^{ig} - RT - h + Pv}{v}\right)^{1/2} \qquad (22\text{-}9)$$

where u is the internal energy, v is the molar volume, h is the enthalpy, and the superscript ig refers to the ideal gas. Similar characteristics are observed for a plot of other density-dependent variables versus pressure, e.g., density, enthalpy, entropy, viscosity, and diffusion coefficient. However, unlike δ, some of these properties decrease with density. The δ for gaseous carbon dioxide is essentially zero; whereas, the value for liquid carbon dioxide is like that of a hydrocarbon. At –30°C there is a large increase in δ upon condensation from vapor to liquid. Above the critical temperature, it is possible to tune the solubility parameter continuously over a wide range with either a small isothermal pressure change or a small isobaric temperature change. This ability to tune the solvent strength of a supercritical fluid is its

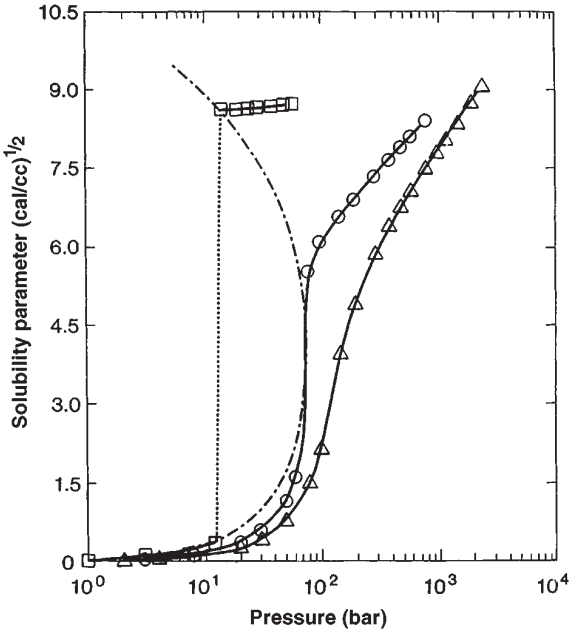


FIG. 22-17 Solubility parameter of CO_2 as a function of pressure in the gas, liquid, and supercritical states (···: –30°C; ○: 31°C; Δ: 70°C).

unique feature, and it can be used to extract and then recover selected products. Note that density and δ are more direct measures of the solvent strength of a SCF than pressure.

Although density (either mass or molar) is a good indicator of solvent strength for a single SCF, it is not a useful indicator for comparing different fluids. For example, CF_3Cl at 40°C and 1300 bar has a mass density of 1.95 g/cm^3, yet it is a weaker solvent than the much less dense fluid SCF CO_2 or liquid hexane. The same argument applies for SF_6. A better indicator of the van der Waals forces contributed by a SCF is obtained by multiplying ρ by the molecular polarizability, α, which is a constant for a given molecule. The solubility parameter δ of CO_2 can be misleading. It is larger than ethane's even though ethane has a larger value of αρ. However about 20 percent of δ for CO_2 may be attributed to its large quadrupole moment. For nonpolar solutes, where this quadrupole moment is unimportant, CO_2 is a much weaker solvent than *n*-hexane, and is more like fluorocarbons, which also have small values of αρ.

Water, a key SCF, undergoes profound changes upon heating to the critical point. It expands by a factor of 3 destroying about ⅔ of the hydrogen bonds, and the dielectric constant drops from 80 to 5 (Shaw et al., op. cit.). (See Fig. 22-18.) *Supercritical water* (SCW) therefore behaves like a "nonaqueous" solvent, and it dissolves many organics and even gases such as O_2. At 400°C and 350 bar, the density of water is 0.47 g/mL, the dielectric constant, ε, is 10, and the ion product, K_w, is 7×10^{-14} compared with 10^{-14} at room temperature. Here, water behaves as a dense fluid which can dissolve electrolytes, with high diffusion coefficients and ion mobilities. At 500°C and the same pressure, the density of water is only 0.144 g/mL, ε is 2, and K_w is 2×10^{-20}. At these conditions, water is a high-temperature gas which does not solvate ions significantly.

Transport Properties Although the densities of supercritical fluids approach those of conventional liquids, their transport properties are closer to those of gases, as shown for a typical SCF such as CO_2 in Table 22-12. For example, the viscosity is several orders of magnitude lower than at liquidlike conditions. The self-diffusion coefficient ranges between 10^{-3} and 10^{-5} cm^2/s, and binary-diffusion coefficients are similar [Liong, Wells, and Foster, *J. Supercritical Fluids* **4,** 91 (1991); Catchpole and King, *Ind. Eng. Chem. Research,* **33,** 1828 (1994)]. These values are as much as one hundred times larger than those typically observed in conventional liquids. The improved transport rates in SCFs versus liquid solvents are important in practical applications including supercritical extraction. Furthermore, carbon dioxide diffuses through condensed-liquid phases (e.g., adsorbents and polymers) faster than do typical solvents which have larger molecular sizes.

TABLE 22-12 Density and Transport Properties of a Gas, Supercritical Fluid, and a Liquid

State	ρ (g/cm^3)	μ (g/cm·s)	D (cm^2/s)
Gas, 1 bar	10^{-3}	10^{-4}	0.2
SCF (T_c, P_c)	0.3	10^{-4}	10^{-3}
Liquid	1	10^{-2}	10^{-5}

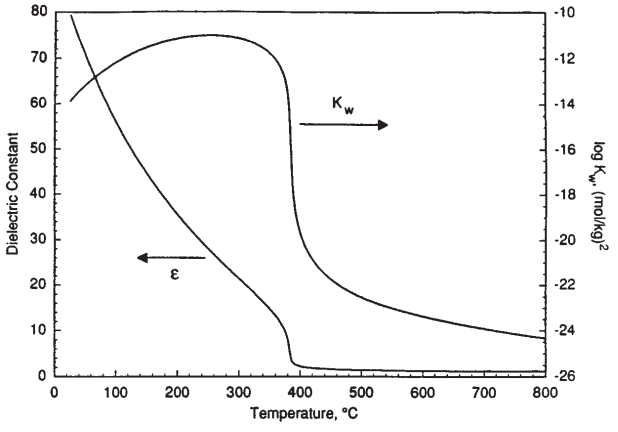


FIG. 22-18 Dielectric constant and dissociation constant, K_w, of water at 250 bar (*Tester et al., op. cit.*).

PROCESS CONCEPTS IN SUPERCRITICAL FLUID EXTRACTION

Figure 22-19 shows a one-stage extraction process that utilizes the adjustability of the solvent strength with pressure in a separation process. The solvent flows through the extraction chamber at a relatively high pressure to extract the components of interest from the feed. The products are then recovered in the separator by depressurization, and the solvent is recompressed and recycled. The products can also be precipitated from the extract phase by raising the temperature after the extraction to lower the solvent density. In the increasing pressure profiling approach, conditions are set so that only the lightest components in the feed are extracted in the first fraction. The recovery vessel is then replaced, and the pressure is increased to collect the next heavier fraction. In the multistage isothermal decreasing pressure profiling process, all but the heaviest fraction are extracted in the first vessel. The extract then passes through a series of recovery vessels held at successively lower pressures, each of which precipitates the next lower molecular-weight fraction in the raffinate. A new process, critical isobaric temperature-rising elution fractionation, is a supercritical variation on temperature-rising elution fractionation in a liquid solvent (McHugh and Krukonis, op. cit.).

Solids may be processed continuously or semicontinuously by pumping slurries or by using lock hoppers. An example is the separation of insoluble polymers by floatation with a variable-density SCF. For liquid feeds, multistage separation may be achieved by continuous counter-current extraction, much like conventional liquid-liquid extraction. The final products may be recovered from the extract phase by a depressurization, a temperature change, or by conventional distillation.

PHASE EQUILIBRIA

Liquid-Fluid Equilibria Nearly all binary liquid-fluid phase diagrams can be conveniently placed in one of six classes (Fig. 22-20). Two-phase regions are represented by an area and three-phase regions by a line. In Class I, the two components are completely miscible, and a single critical mixture curve connects their critical points. Class II behavior is similar, except that a region of liquid-liquid immiscibility is found at lower temperatures. As the two components become increasingly dissimilar, the *upper critical solution temperature* (UCST) line merges with the branch of the critical mixture curve that begins at the heavier component's critical point, and Class III

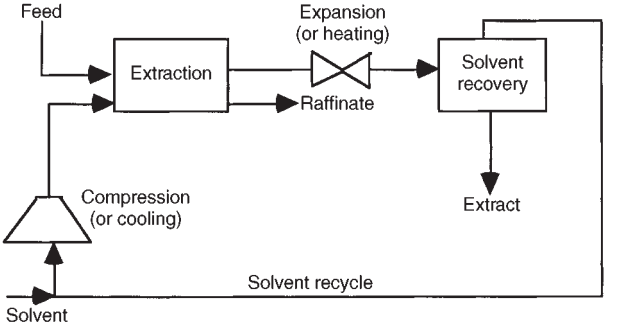


FIG. 22-19 Schematic diagram of a typical supercritical fluid-extraction process.

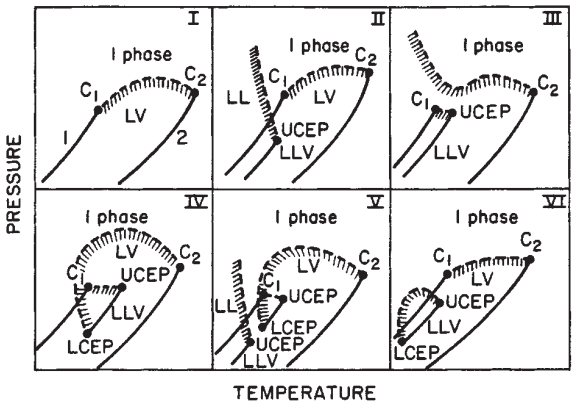


FIG. 22-20 Six classes of binary liquid-fluid phase diagrams (*Prausnitz et al.,* Molecular Thermodynamics of Fluid-Phase Equilibria, © *1986. Reprinted by permission of Prentice-Hall, Inc.*).

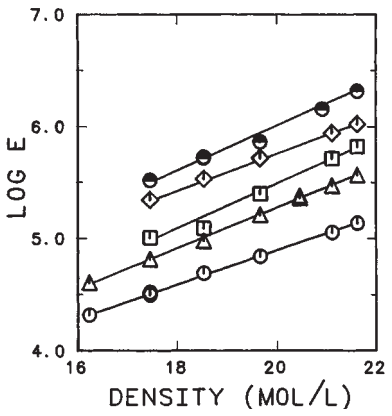


FIG. 22-21 Enhancement factor for solids with a variety of polar functionalities in CO_2 at 35°C (from bottom to top: hexamethylbenzene, 2-naphthol, phthalic anhydride, anthracene, acridine).

behavior is observed. In Class IV behavior, the mixture critical curve bends down to low pressures and intercepts the three-phase *liquid-liquid-vapor* (LLV) line at the lower critical end point. Class V resembles Class IV except it includes an additional LL critical curve. Class VI has features of Class II except that the critical curve intersects the LLV line twice.

For a ternary system, the phase diagram appears much like that in conventional liquid-liquid equilibrium. However, because a SCF solvent is compressible, the slopes of the tie lines (distribution coefficients) and the size of the two-phase region can vary significantly with pressure as well as temperature. Furthermore, at lower pressures, LLV tie-triangles appear upon the ternary diagrams and can become quite large.

Solid-Fluid Equilibria The phase diagrams of binary mixtures in which the heavier component (the solute) is normally a solid at the critical temperature of the light component (the solvent) include *solid-liquid-vapor* (SLV) curves which may or may not intersect the LV critical curve. The solubility of the solid is very sensitive to pressure and temperature in compressible regions where the solvent's density and solubility parameter are highly variable. In contrast, plots of the log of the solubility versus density at constant temperature exhibit fairly simple linear behavior.

To understand the role of solute-solvent interactions on solubilities and selectivities, it is instructive to define an enhancement factor, E, as the actual solubility, y_2, divided by the solubility in an ideal gas, so that $E = y_2P/P_2^{sat}$, where P_2^{sat} is the vapor pressure. This factor is a normalized solubility because it removes the effect of the vapor pressure, providing a means to focus on interactions in the SCF phase. For a given fluid at a particular temperature and pressure, enhancement factors do not vary much for many types of organic solids of similar molecular weight. As shown in Fig. 22-21, Es fall within a range of only about 1.5 orders of magnitude for substances with a variety of polar functional groups, even though the actual solubilities (not shown) vary by many orders of magnitude. This means that solubilities, and also selectivities, in carbon dioxide are governed primarily by vapor pressures and only secondarily by solute-solvent interactions in the SCF phase. However, fluid-phase interactions can be especially important if cosolvents are added which are strong Lewis acids or bases.

Polymer-Fluid Equilibria and the Glass Transition Most polymer systems fall in the Class III or Class V phase diagrams, and the same system can often change from one class into the other as the polymer's molecular weight changes. Most polymers are insoluble in CO_2 below 100°C, yet CO_2 can be quite soluble in the polymer. For example, the sorption of CO_2 into silicone rubber is highly dependent upon temperature and pressure, since these properties have a large influence on the density and activity of CO_2.

For glassy polymers, sorption isotherms are more complex and hysteresis between the pressurization and depressurization steps may appear. CO_2 adds free volume to the polymer that can relax very slowly. Furthermore, CO_2 can act as a plasticizer and depress the glass transition temperature by 100°C or even more. Not only do the mechanical properties change as the polymer is plasticized, but the diffusion coefficient of CO_2 and other solutes can increase by orders of magnitude. In PMMA, for instance, carbon dioxide's diffusion coefficient increases by as much as two orders-of-magnitude as the pressure is increased by 75 bar at 35°C.

Cosolvents and Surfactants Many nonvolatile polar substances cannot be dissolved at moderate temperatures in nonpolar fluids such as CO_2. Cosolvents (also called entrainers, modifiers, moderators) such as alcohols and acetone have been added to fluids to raise the solvent strength. The addition of only 2 mol % of the complexing agent tri-*n*-butyl phosphate (TBP) to CO_2 increases the solubility of hydroquinone by a factor of 250 due to Lewis acid-base interactions. Very recently, surfactants have been used to form reverse micelles, microemulsions, and polymeric latexes in SCFs including CO_2. These organized molecular assemblies can dissolve hydrophilic solutes and ionic species such as amino acids and even proteins. Examples of surfactant tails which interact favorably with CO_2 include fluoroethers, fluoroacrylates, fluoroalkanes, propylene oxides, and siloxanes.

Phase Equilibria Models Two approaches are available for modeling the fugacity of a solute, f_i, in a supercritical fluid solution. The compressed gas approach is the most common where:

$$f_i^G = y_i \phi_i P \tag{22-10}$$

and ϕ_i is the fugacity coefficient of component i. The "expanded liquid" approach is given as:

$$f_i^L = x_i \gamma_i (P^0, x_i) f_i^{0L}(P^0) \exp\left\{\int_{P^0}^{P} \frac{\bar{v}_i}{RT}\, dP\right\} \tag{22-11}$$

where x_i is the mole fraction, γ_i is the activity coefficient, P^0 and f_i^0 are the reference pressure and fugacity, respectively, and $\bar{v}_i$ is the partial molar volume of component i. In principle this approach has an advantage in that γ_i can be chosen to give exact results at a pressure in the near-critical region, but the use of γ_i introduces an additional parameter.

A variety of equations-of-state have been applied to supercritical fluids, ranging from simple cubic equations like the Peng-Robinson equation-of-state to the Statistical Associating Fluid Theory. All are able to model nonpolar systems fairly successfully, but most are increasingly challenged as the polarity of the components increases. The key is to calculate the solute-fluid molecular interaction parameter from the pure-component properties. Often the standard approach (i.e. corresponding states based on critical properties) is of limited accuracy due to the vastly different critical temperatures of the solutes (if known) and the solvents; other properties of the solute

are more appropriate [Johnston et al., *Ind. Eng. Chem. Research.*, **28,** 1115 (1989)].

MASS TRANSFER

Experimental gas-solid mass-transfer data have been obtained for naphthalene in CO_2 to develop correlations for mass-transfer coefficients [Lim et al., *Am. Chem. Soc. Symp. Ser.*, **406,** 379 (1989)]. The data were correlated over a wide range of conditions with the following equation for combined natural and forced convection:

$$\mathrm{Sh}/(\mathrm{Sc}\cdot\mathrm{Gr})^{1/4} = e(\mathrm{Re}/\mathrm{Gr}^{1/2})^{f} \qquad (22\text{-}12)$$

where Sh, Sc, Gr, and Re are the Sherwood, Schmidt, Grashof, and Reynolds numbers, respectively, and e and f are constants. The mass-transfer coefficient increases dramatically near the critical point, goes through a maximum and then decreases gradually. The strong natural convection at SCF conditions leads to higher mass-transfer rates than in liquid solvents.

A comprehensive mass-transfer model has been developed for SCF extraction from an aqueous phase to CO_2 in countercurrent sieve tray and packed columns [Seibert and Moosberg, *Sep. Sci. Technol.*, **23,** 2049 (1988)]. Both the hydraulics and mass-transfer coefficients were obtained from models developed for conventional liquid extraction, and the results were in good agreement with experiment for a 10-cm diameter column either with sieve trays or packing. If interfacial tensions are comparable, mass-transfer rates for extraction of organics from aqueous solutions are higher for CO_2 than hydrocarbon solvents. For this type of extraction, it was found that CO_2 preferentially wets ceramic and metal packings; consequently, trays are more efficient than packings.

APPLICATIONS

Food and Pharmaceutical Applications These applications are driven by the environmental acceptability of CO_2, as well as by the ability to tailor the extraction with the adjustable solvent strength. The General Foods coffee decaffeination plant in Houston, Texas is designed to process between 15,000 and 30,000 pounds of coffee beans per hour (McHugh and Krukonis, op. cit.). See Fig. 22-22. The moist, green coffee beans are charged to an extraction vessel approximately 7 ft diameter by 70 ft high, and carbon dioxide is used to extract the caffeine from the beans. Various methods have been proposed for recovery of the caffeine including washing with water and adsorption. Often the recovery of a particular component of an extract is the key challenge in SCF extraction. Thus, SCF extraction is frequently combined with another process such as distillation, absorption, or adsorption.

Temperature-Controlled Residuum Oil Supercritical Extraction (ROSE) The Kerr-McGee ROSE process has been licensed by over a dozen companies worldwide. The extraction step uses a liquid solvent, and the solvent is recovered at supercritical conditions to save energy as shown in Fig. 22-23. The residuum is contacted with butane or pentane to precipitate the heavy asphaltene fraction. The extract is then passed through a series of heaters, where it goes from the liquid state to a lower-density supercritical fluid state. Because the entire process is carried out at conditions near the critical point, a relatively small temperature change is required to produce a fairly large density change. After the light oils have been removed, the solvent is cooled back to the liquid state and recycled.

Extraction from Aqueous Solutions Critical Fluid Technologies, Inc. has developed a continuous countercurrent extraction process based on a 0.5- by 10-m column to extract residual organic solvents such as trichloroethylene, methylene chloride, benzene, and chloroform from industrial wastewater streams. Typical solvents include supercritical CO_2 and near-critical propane. The economics of these processes are largely driven by the hydrophilicity of the product, which has a large influence on the distribution coefficient. For example, at 16°C, the partition coefficient between liquid CO_2 and water is 0.4 for methanol, 1.8 for *n*-butanol, and 31 for *n*-heptanol.

Adsorption and Desorption Adsorbents may be used to recover solutes from supercritical fluid extracts; for example, activated carbon and polymeric sorbents may be used to recover caffeine from CO_2. This approach may be used to improve the selectivity of a supercritical fluid extraction process. SCF extraction may be used to regenerate adsorbents such as activated carbon and to remove contaminants from soil. In many cases the chemisorption is sufficiently strong that regeneration with CO_2 is limited, even if the pure solute is quite soluble in CO_2. In some cases a cosolvent can be added to the SCF to displace the sorbate from the sorbent. Another approach is to use water at elevated or even supercritical temperatures to facilitate desorption. Many of the principles for desorption are also relevant to extraction of substances from other substrates such as natural products and polymers.

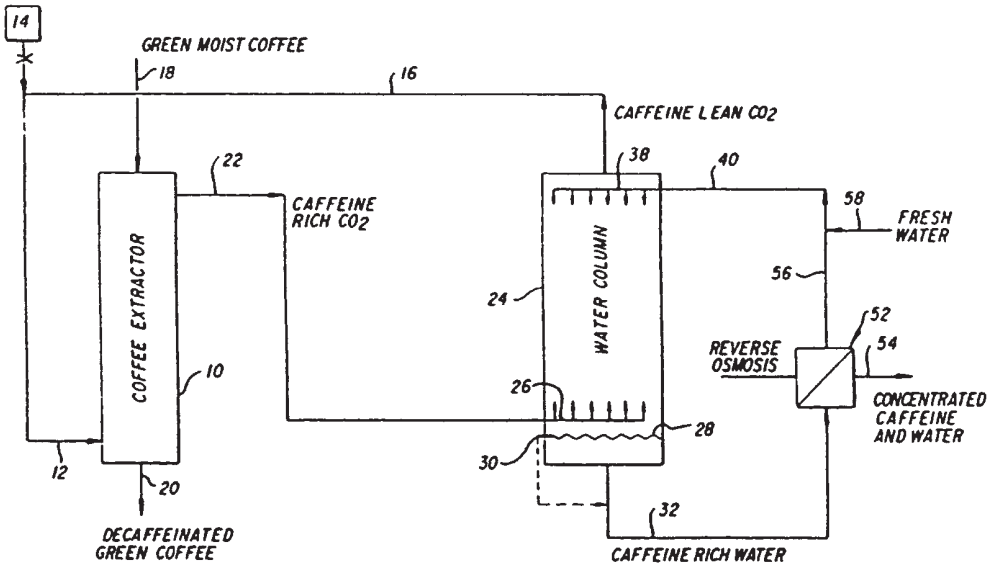


FIG. 22-22 Schematic diagram of the Kraft process for producing decaffeinated coffee using supercritical carbon dioxide (*McHugh and Krukonis, op. cit.*).

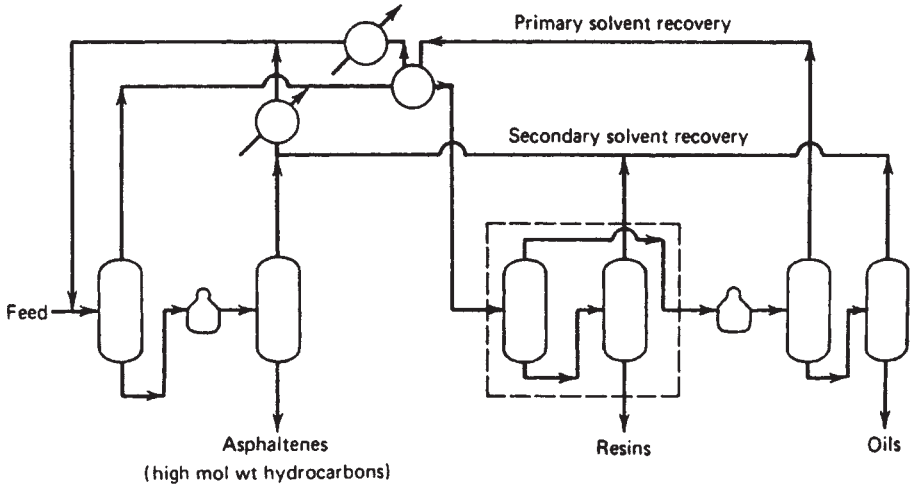


FIG. 22-23 Schematic diagram of the Kerr-McGee ROSE process.

Polymer Devolatilization and Fractionation Supercritical fluids may be used to extract solvent, monomers, and oligomers from polymers. After extraction the pressure is reduced to atmospheric leaving little residue in the substrate; furthermore, the extracted impurities are easily recovered from the SCF. To aid process design, partition coefficients of various solutes between polymers and CO_2 have been measured with static and dynamic techniques such as inverse supercritical fluid chromatography. The swelling and lowering of the glass transition temperature of the polymer by the SCF can increase mass-transfer rates markedly. The polymer may or may not return to its original dimensions, depending upon factors such as the glass transition properties and crystallinity.

Supercritical fluids may be used to fractionate polymers on the basis of molecular weight and/or composition. The most common techniques are isothermal increasing-pressure profiling and isothermal decreasing-pressure profiling as discussed in the above section on process concepts. The critical isobaric temperature rising elution fractionation process can be used to fractionate polymers as a function of crystallinity (e.g., due to branching), based on the melting points in the presence of the fluid (McHugh and Krukonis, op. cit.).

Drying and Aerogel Formation One of the oldest practical applications of supercritical fluids, developed in 1932, is supercritical fluid drying. Here the solvent is extracted from a porous solid with a SCF fluid, and then the fluid is depressurized. Because the fluid expands from the solid without crossing a liquid-vapor phase boundary, capillary forces are not present which would otherwise collapse the structure. Using supercritical fluid drying, aerogels have been prepared with densities so low that they essentially float in air and look like a cloud of smoke. The process is used in a commercial instrument to dry samples for electron microscopy without perturbing the structure.

Cleaning Supercritical fluids such as CO_2 are being used to clean and degrease quartz rods used to produce optical fibers, products used in the fabrication of printed circuit boards, oily chips from machining operations, and precision bearings in military applications, and so on. Here, CO_2 replaces conventional chlorocarbon or chlorofluorocarbon solvents.

Analytical Supercritical Fluid Extraction and Chromatography Supercritical fluids, especially CO_2, are used widely to extract a wide variety of solid and liquid matrices to obtain samples for analysis. Benefits compared with conventional Soxhlet extraction include minimization of solvent waste, faster extraction, tunability of solvent strength, and simple solvent removal with minimal solvent contamination in the sample. Compared with high-performance liquid chromatography, the number of theoretical stages is higher in SCF chromatography due to the more favorable transport rates. A limitation in each of these applications is the low solvent strength of CO_2; often cosolvents are required.

Precipitation with a Compressed Fluid Antisolvent (PCA) Because fluids such as CO_2 are weak solvents, they are often more effective as antisolvents. In this process, the antisolvent may be a compressed gas, pressurized liquid, or a supercritical fluid. Mixing of a solution with the antisolvent leads to a precipitated product. There are two primary process configurations for this mixing: (1) a pure, compressed fluid may be added to a liquid solution or (2) a liquid solution may be sprayed through a nozzle into a pure, compressed fluid. Gaseous CO_2 is quite soluble in a number of organic solvents such as methanol, toluene, dimethylformamide, and tetrahydrofuran, at pressures from 10 to 100 bar. As CO_2 mixes with the liquid phase, it decreases the cohesive energy density (solvent strength) substantially, leading to precipitation of dissolved solutes (e.g., crystals of progesterone). It has been demonstrated that the rate of addition of a fluid antisolvent or the liquid solvent may be programmed to control crystal morphology, size, and size distribution over a wide range from 1 to 100 μm. The high-diffusion rates of the organic solvent into CO_2 and vice-versa can lead to rapid-phase separation. This process may be used to precipitate a solute from a solvent or for separation of solutes.

Crystallization Solutes may be crystallized from supercritical fluids by temperature and/or pressure changes, and by the PCA process described above. In the *rapid expansion from supercritical solution* (RESS) process, a SCF containing a dissolved solute is expanded through a nozzle or orifice in less than 1 ms to form small particles or fibers. A variety of inorganic crystals have been formed naturally and synthetically in SCF water.

Reactive Separations Reactions may be integrated with SCF separation processes to achieve a large degree of control for producing a highly purified product. Reaction products may be recovered by volatilization into, or precipitation from, a SCF phase. A classic example is the high-pressure production of polyethylene in the reacting solvent SCF ethylene. The molecular-weight distribution may be controlled by choosing the temperature and pressure for precipitating the polymer from the SCF phase.

In the last few years, Idemitsu commercialized a 5000 metric ton/year integrated reaction and separation process in SCF isobutene, as shown in Fig. 22-24. The reaction of isobutene and water takes place in the water phase and is acid catalyzed. The product, *sec*-butanol, is extracted into the isobutene phase to drive the reversible reaction to the right. The *sec*-butanol is then recovered from the isobutene by depressurizing the SCF phase, and the isobutene is recompressed and recycled.

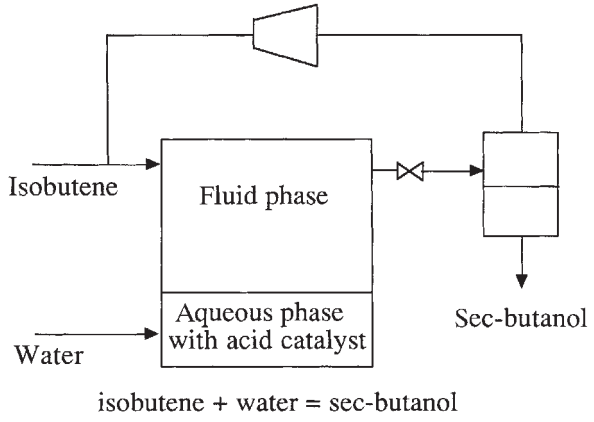


FIG. 22-24 Process for the integrated reaction and separation of *sec*-butanol from isobutene.

Supercritical fluid solvents have been tested for reactive extractions of liquid and gaseous fuels from heavy oils, coal, oil shale, and biomass. In some cases the solvent participates in the reactions, as in the hydrolysis of coal and heavy oils with water. Related applications include conversion of cellulose to glucose in water, delignification of wood with ammonia, and liquefaction of lignin in water.

Hydrothermal oxidation (HO) (also called supercritical water oxidation) is a reactive process to separate aqueous wastes into water, CO_2, nitrogen, salts, and other byproducts. It is an enclosed and complete water-treatment process making it more desirable to the public than incineration (Fig. 22-25) (Tester et al., op. cit.; Gloyna and Li, op. cit.; Shaw et al., op. cit.). As mentioned above, organics and oxygen mix in a single phase in SCW due the low dielectric constant. Oxidation is rapid and efficient in this one-phase solution, so that wastewater containing 1 to 20 wt % organics may be oxidized rapidly in SCW with higher energy efficiency and much less air pollution than in conventional incineration. Temperatures range from about 375 to 650°C and pressures from 3000 to about 5000 psia. Conversions can be greater than 99.99 percent for reactor residence times of a minute or less. Organics are oxidized to CO_2, H_2O, and molecular nitrogen with little NO_x. A commercial plant designed by Eco-Waste Technology appeared in Austin, Texas in 1994.

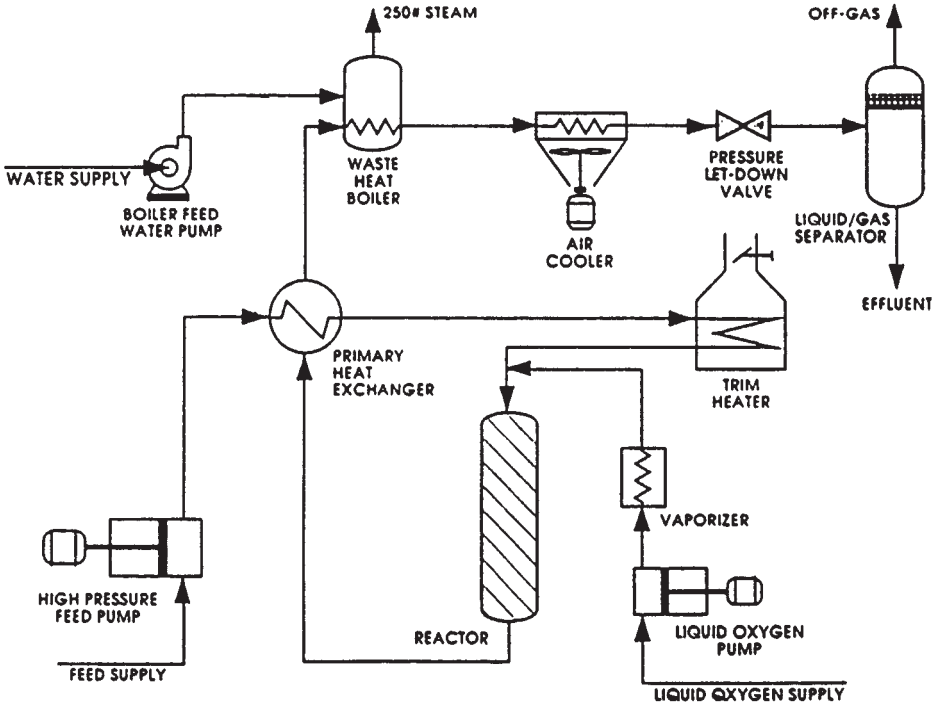


FIG. 22-25 Hydrothermal-oxidation process (also called supercritical water oxidation) for wastewater purification. *(Courtesy Eco-Waste Technologies.)*

ALTERNATIVE SOLID/LIQUID SEPARATIONS

SEPARATION PROCESSES BASED PRIMARILY ON ACTION IN AN ELECTRIC FIELD

Differences in mobilities of ions, molecules, or particles in an electric field can be exploited to perform useful separations. Primary emphasis is placed on electrophoresis and dielectrophoresis. Analogous separation processes involving magnetic and centrifugal force fields are widely applied in the process industry (see Secs. 18 and 19).

Theory of Electrical Separations

General References: Newman, *Adv. Electrochem. Electrochem. Eng.*, **5,** 87 (1967); *Ind. Eng. Chem.*, **60**(4), 12 (1968). Ptasinski and Kerkhof, *Sep. Sci. Technol.*, **27,** 995 (1992).

For electrolytic solutions, migration of charged species in an electric field constitutes an additional mechanism of mass transfer. Thus the flux of an ionic species N_i in (g·mol)/(cm²·s) in dilute solutions can be expressed as

$$N_i = -z_i u_i \mathcal{F} c_i \nabla E - D_i \nabla c_i + c_i v \tag{22-13}$$

The ionic mobility u_i is the average velocity imparted to the species under the action of a unit force (per mole). v is the stream velocity, cm/s. In the present case, the electrical force is given by the product of the electric field ∇E in V/cm and the charge $z_i\mathcal{F}$ per mole, where $\mathcal{F}$ is the Faraday constant in C/g equivalent and z_i is the valence of the ith species. Multiplication of this force by the mobility and the concentration c_i [(g·mol)/cm³] yields the contribution of migration to the flux of the ith species.

The diffusive and convective terms in Eq. (22-13) are the same as in nonelectrolytic mass transfer. The ionic mobility u_i, (g·mol·cm²)/(J·s), can be related to the ionic-diffusion coefficient D_i, cm²/s, and the ionic conductance of the ith species λ_i, cm²/(Ω·g equivalent):

$$u_i = D_i/RT = \lambda_i/|z_i|\mathcal{F}^2 \tag{22-14}$$

where T is the absolute temperature, K; and R is the gas constant, 8.3143 J/(K·mol). Ionic conductances are tabulated in the literature (Robinson and Stokes, *Electrolyte Solutions*, Academic, New York, 1959). For practical purposes, a bulk electrolytic solution is electrically neutral.

$$\sum_i z_i c_i = 0 \tag{22-15}$$

since the forces required to effect an appreciable separation of charge are prohibitively large.

The **current density** (A/cm²) produced by movement of charged species is described by summing the terms in Eq. (22-16) for all species:

$$i = \mathcal{F} \sum_i z_i \mathbf{N}_i = -\kappa \nabla E - \mathcal{F} \sum_i z_i D_i \nabla c_i \tag{22-16}$$

where the electrical conductivity κ in S/cm is given by

$$\kappa = \mathcal{F}^2 \sum_i z_i^2 u_i c_i \tag{22-17}$$

In solutions of uniform composition, the diffusional terms vanish and Eq. (22-16) reduces to Ohm's law.

Conservation of each species is expressed by the relation

$$\partial c_i/\partial t = -\nabla \cdot \mathbf{N}_i \tag{22-18}$$

provided that the species is not produced or consumed in homogeneous chemical reactions. In two important cases, this conservation law reduces to the equation of convective diffusion:

$$(\partial c_i/\partial t) + \mathbf{v}\nabla \cdot c_i = D\,\nabla^2 c_i \tag{22-19}$$

First, when a large excess of inert electrolyte is present, the electric field will be small and migration can be neglected for minor ionic components; Eq. (22-19) then applies to these minor components, where D is the ionic-diffusion coefficient. Second, Eq. (22-19) applies when the solution contains only one cationic and one anionic species. The electric field can be eliminated by means of the electroneutrality relation.

In the latter case the diffusion coefficient D of the electrolyte is given by

$$D = (z_+u_+D_- - z_-u_-D_+)/(z_+u_+ - z_-u_-) \tag{22-20}$$

which represents a compromise between the diffusion coefficients of the two ions. When Eq. (22-19) applies, many solutions can be obtained by analogy with heat transfer and nonelectrolytic mass transfer.

Because the solution is electrically neutral, conservation of charge is expressed by differentiating Eq. (22-16):

$$\nabla \cdot \mathbf{i} = 0 = -\kappa \nabla^2 E - \mathcal{F} \sum_i z_i D_i \nabla^2 c_i \tag{22-21}$$

For solutions of uniform composition, Eq. (22-21) reduces to Laplace's equation for the potential:

$$\nabla^2 E = 0 \tag{22-22}$$

This equation is the starting point for determination of the current-density distributions in many electrochemical cells.

Near an interface or at solution junctions, the solution departs from electroneutrality. Charges of one sign may be preferentially adsorbed at the interface, or the interface may be charged. In either case, the charge at the interface is counterbalanced by an equal and opposite charge composed of ions in the solution. Thermal motion prevents this countercharge from lying immediately adjacent to the interface, and the result is a "diffuse-charge layer" whose thickness is on the order of 10 to 100 Å.

A tangential electric field ∇E_t acting on these charges produces a relative motion between the interface and the solution just outside the diffuse layer. In view of the thinness of the diffuse layer, a balance of the tangential viscous and electrical forces can be written

$$\mu(\partial^2 v_t/\partial y^2) + \rho_e \nabla E_t = 0 \tag{22-23}$$

where μ is the viscosity and ρ_e is the electric-charge density, C/cm³. Furthermore, the variation of potential with the normal distance satisfies Poisson's equation:

$$\partial^2 E/\partial y^2 = -(\rho_e/\varepsilon) \tag{22-24}$$

with ε defined as the **permittivity** of the solution. [The relative dielectric constant is $\varepsilon/\varepsilon_0$, where ε_0 is the permittivity of free space; $\varepsilon_0 = 8.8542 \times 10^{-14}$ C/(V·cm).] Elimination of the electric-charge density between Eqs. (22-23) and (22-24) with two integrations, gives a relation between ∇E_t and the velocity v_0 of the bulk solution relative to the interface.

$$\mu[v_t(\infty) - v_t(0)] = \varepsilon \nabla E_t [E(\infty) - E(0)] \tag{22-25}$$

or

$$v_0 = -(\varepsilon \nabla E_t \zeta/\mu) \tag{22-26}$$

The potential difference across the mobile part of the diffuse-charge layer is frequently called the **zeta potential,** $\zeta = E(0) - E(\infty)$. Its value depends on the composition of the electrolytic solution as well as on the nature of the particle-liquid interface.

There are four related electrokinetic phenomena which are generally defined as follows: *electrophoresis*—the movement of a charged surface (i.e., suspended particle) relative to a stationary liquid induced by an applied electrical field, *sedimentation potential*—the electric field which is crested when charged particles move relative to a stationary liquid, *electroosmosis*—the movement of a liquid relative to a stationary charged surface (i.e., capillary wall), and *streaming potential*—the electric field which is created when liquid is made to flow relative to a stationary charged surface. The effects summarized by Eq. (22-26) form the basis of these electrokinetic phenomena.

For many particles, the diffuse-charge layer can be characterized adequately by the value of the zeta potential. For a spherical particle of radius r_0 which is large compared with the thickness of the diffuse-charge layer, an electric field uniform at a distance from the particle will produce a tangential electric field which varies with position on the particle. Laplace's equation [Eq. (22-22)] governs the distribution

of potential outside the diffuse-charge layer; also, the Navier-Stokes equation for a creeping-flow regime can be applied to the velocity distribution. On account of the thinness of the diffuse-charge layer, Eq. (22-26) can be used as a local boundary condition, accounting for the effect of this charge in leading to movement of the particle relative to the solution. The result of this computation gives the velocity of the particle as

$$v = \varepsilon\zeta\, \nabla E/\mu \qquad (22\text{-}27)$$

and it may be convenient to tabulate the mobility of the particle

$$U = v/\nabla E = \varepsilon\zeta/\mu \qquad (22\text{-}28)$$

rather than its zeta potential. Note that this mobility gives the velocity of the particle for unit electric field rather than for unit force on the particle. Related equations can be developed for the velocity of electroosmotic flow. The subsections presented below ("Electrophoresis," "Electrofiltration," and "Cross-Flow–Electrofiltration") represent both established and emerging commercial applications of electrokinetic phenomena.

Electrophoresis

General Reference: Wankat, *Rate-Controlled Separations,* Elsevier, London, 1990.

Electrophoretic Mobility Macromolecules move at speeds measured in tenths of micrometers per second in a field (gradient) of 1 V/cm. Larger particles such as bubbles or bacteria move up to 10 times as fast because U is usually higher. To achieve useful separations, therefore, voltage gradients of 10 to 100 V/cm are required. High voltage gradients are achieved only at the expense of power dissipation within the fluid, and the resulting heat tends to cause undesirable convection currents.

Several devices are available commercially to measure mobility. One of these (Zeta-Meter Inc., New York) allows direct microscopic measurement of individual particles. Another allows measurement in more concentrated suspensions (Numinco Instrument Corp., Monroeville, Pa.). The state of the charge can also be measured by a streaming-current detector (Waters Associates, Inc., Framingham, Mass.). For macromolecules, more elaborate devices such as the Tiselius moving-boundary apparatus are used.

Mobility is affected by the dielectric constant and viscosity of the suspending fluid, as indicated in Eq. (22-28). The ionic strength of the fluid has a strong effect on the thickness of the double layer and hence on ζ. As a rule, mobility varies inversely as the square root of ionic strength [Overbeek, *Adv. Colloid Sci.,* **3,** 97 (1950)].

Modes of Operation There is a close analogy between sedimentation of particles or macromolecules in a gravitational field and their electrophoretic movement in an electric field. Both types of separation have proved valuable not only for analysis of colloids but also for preparative work, at least in the laboratory. Electrophoresis is applicable also for separating mixtures of simple cations or anions in certain cases in which other separating methods are ineffectual.

Electrodecantation or electroconvection is one of several operations in which one mobile component (or several) is to be separated out from less mobile or immobile ones. The mixture is introduced between two vertical semipermeable membranes; for separating cations, anion membranes are used, and vice versa. When an electric field is applied, the charged component migrates to one or another of the membranes; but since it cannot penetrate the membrane, it accumulates at the surface to form a dense concentrated layer of particles which will sink toward the bottom of the apparatus. Near the top of the apparatus immobile components will be relatively pure. Murphy [*J. Electrochem. Soc.,* **97**(11), 405 (1950)] has used silver-silver chloride electrodes in place of membranes. Frilette [*J. Phys. Chem.,* **61,** 168 (1957)], using anion membranes, partially separated H^+ and Na^+, K^+ and Li^+, and K^+ and Na^+. Unfortunately no simple electrodecantation apparatus is available for bench-scale testing. A rather complex device described by Polson and Largier [in Alexander and Block (eds.), *Analytical Methods of Protein Chemistry,* vol. I, Pergamon, New York, 1960] is available commercially (Quickfit Reeve Angel, Inc., Clifton, NJ).

Countercurrent electrophoresis can be used to split a mixture of mobile species into two fractions by the electrical analog of elutriation. In such countercurrent electrophoresis, sometimes termed an ion still, a flow of the suspending fluid is maintained parallel to the direction of the voltage gradient. Species which do not migrate fast enough in the applied electric field will be physically swept out of the apparatus. An apparatus based mainly on this principle but using also natural convection currents has been developed (Bier, *Electrophoresis,* vol. II, Academic, New York, 1967).

Membrane electrophoresis which is based upon differences in ion mobility, has been studied by Glueckauf and Kitt [*J. Appl. Chem.,* **6,** 511 (1956)]. Partial exclusion of coions by membranes results in large differences in coion mobilities. Superposing a cation and an anion membrane gives high transference numbers (about 0.5) for both cations and anions while retaining the selectivity of mobilities. Large voltages are required, and flow rates are low.

In continuous-flow zone electrophoresis the "solute" mixture to be separated is injected continuously as a narrow source within a body of carrier fluid flowing between two electrodes. As the "solute" mixture passes through the transverse field, individual components migrate sideways to produce zones which can then be taken off separately downstream as purified fractions.

Resolution depends upon differences in mobilities of the species. Background electrolyte of low ionic strength is advantageous, not only to increase electrophoretic (solute) mobilities, but also to achieve low electrical conductivity and thereby to reduce the thermal-convection current for any given field [Finn, in Schoen (ed.), *New Chemical Engineering Separation Techniques,* Interscience, New York, 1962].

The need to limit the maximum temperature rise has resulted in two main types of apparatus, illustrated in Fig. 22-26. The first consists of multicomponent ribbon separation units—apparatus capable of separating small quantities of mixtures which may contain few or many species. In general, such units operate with high voltages, low currents, a large transverse dimension, and a narrow thickness between cooling faces. Numerous units developed for analytic chemistry, generally with filter-paper curtains but sometimes with granular "anticonvectant" packing, are of this type. The second type consists of block separation units—apparatus designed to separate larger quantities of a mixture into two (or at most three) species or fractions. Such units generally use low to moderate voltages and high currents, with cooling by circulation of cold electrolyte through the electrode compartments. Scale-up can readily be accomplished by extending the thickness dimension w.

Both types of units have generally been operated in trace mode; that is, "background" or "elutant" electrolyte is fed to the unit along with the mixture to be separated. A desirable and possible means of

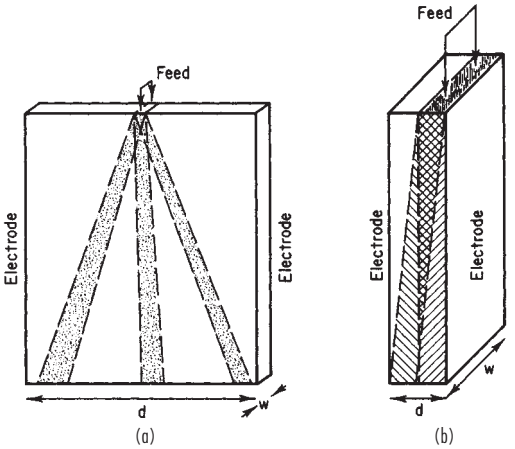


FIG. 22-26 Types of arrangement for zone electrophoresis or electrochromatography. (*a*) Ribbon unit, with $d > w$; cooling at side faces. (*b*) Block unit, with $w > d$; cooling at electrodes.

operation for preparative applications is in bulk mode, in which one separated component follows the other without background electrolyte being present, except that other ions may be required to bracket the separated zones. Overlap regions between components should be recycled, and pure components collected as products.

For block units, the need to stabilize flow has given rise to a number of distinct techniques.

Free flow. Dobry and Finn [*Chem. Eng. Prog.*, **54,** 59 (1958)] used upward flow, stabilized by adding methyl cellulose, polyvinyl alcohol, or dextran to the background solution. Upward flow was also used in the electrode compartments, with cooling efficiency sufficient to keep the main solution within 1°C of entering temperature.

Density gradients to stabilize flow have been employed by Philpot [*Trans. Faraday Soc.*, **36,** 38 (1940)] and Mel [*J. Phys. Chem.*, **31,** 559 (1959)]. Mel's Staflo apparatus [*J. Phys. Chem.*, **31,** 559 (1959)] has liquid flow in the horizontal direction, with layers of increasing density downward produced by sucrose concentrations increasing to 7.5 percent. The solute mixture to be separated is introduced in one such layer. Operation at low electrolyte concentrations, low voltage gradients, and low flow rates presents no cooling problem.

Packed beds. A packed cylindrical electrochromatograph 9 in (23 cm) in diameter and 48 in (1.2 m) high, with operating voltages in the 25- to 100-V range, has been developed by Hybarger, Vermeulen, and coworkers [*Ind. Eng. Chem. Process Des. Dev.*, **10,** 91 (1971)]. The annular bed is separated from inner and outer electrodes by porous ceramic diaphragms. The unit is cooled by rapid circulation of cooled electrolyte between the diaphragms and the electrodes.

An interesting modification of zone electrophoresis resolves mixtures of ampholytes on the basis of **differing isoelectric points** rather than differing mobilities. Such **isoelectric spectra** develop when a pH gradient is established parallel to the electric field. Each species then migrates until it arrives at the region of pH where it possesses no net surface charge. A strong focusing effect is thereby achieved [Kolin, in Glick (ed.), *Methods of Biochemical Analysis*, vol. VI, Interscience, New York, 1958].

Electrofiltration

General Reference: P. Krishnaswamy and P. Klinkowski, "Electrokinetics and Electrofiltration," in *Advances in Solid-Liquid Separation,* H. S. Muralidhara (ed.), Battelle Press, Columbus, OH, 1986.

Process Concept The application of a direct electric field of appropriate polarity when filtering should cause a net charged-particle migration relative to the filter medium (electrophoresis). The same direct electric field can also be used to cause a net fluid flow relative to the pores in a fixed filter cake or filter medium (electroosmosis). The exploitation of one or both of these phenomena form the basis of conventional electrofiltration.

In conventional filtration, often the object is to form a high-solids-content filter cake. At a single-filter surface, a uniform electric field can be exploited in one of two ways. The first method of exploitation occurs when the electric field is of a polarity such that the charged-particle migration occurs toward the filter medium. In this case, the application of the electric field increases the velocity of the solid particles toward the filter surface (electrosedimentation), thereby hastening the clarification of the feed suspension and, at the same time, increasing the compaction of the filter cake collected on the filter surface. In this first case, electroosmotic flow occurs in a direction away from the filter media. The magnitude of the pressure-driven fluid flow toward the filter surface far exceeds the magnitude of the electroosmotic flow away from the surface so that the electroosmotic flow results in only a minor reduction of the rate of production of filtrate. The primary benefits of the applied electric field in this case are increased compaction, and hence increased dewatering, of the filter cake and an increased rate of sedimentation or movement of the particles in bulk suspension toward the filter surface.

The second method of exploitation occurs when the electric field is of a polarity such that the charged-particle migration occurs away from the filter medium. The contribution to the net-particle velocity of the electrophoretically induced flow away from the filter medium is generally orders of magnitude less than the contribution to the net-particle velocity of the flow induced by drag due to the pressure-induced flow of the bulk liquid toward the filter media. (In conventional or cake filtration, the velocity of liquid in dead-end flow toward the filter is almost always sufficient to overcome any electrophoretic migration of particles away from the filter media so that the prevention of the formation of filter cake is not an option. This will not necessarily be the case for cross-flow electrofiltration.) The primary enhancement to filtration caused by the application of an electrical field in this manner is the increase in the filtrate flux due to electroosmotic flow through the filter cake. This electroosmotic flow is especially beneficial during the latter stages of filtration when the final filter-cake thickness has been achieved. At this stage, electroosmosis can be exploited to draw filtrate out from the pore structure of the filter cake. This type of drying of the filter cake is sometimes called **electroosmotic dewatering.**

Commercial Applications Krishnaswamy and Klinkowski, op. cit., describe the Dorr-Oliver EAVF®. The EAVF® combines vacuum filtration with electrophoresis and electroosmosis and has been described as a series of parallel platelike electrode assemblies suspended in a tank containing the slurry to be separated. When using the EAVF®, solids are collected at both electrodes, one collecting a compacted cake simply by electrophoretic attraction and the second collecting a compacted cake though vacuum filtration coupled with electroosmotic dewatering. Upon the completion of a collection cycle, the entire electrode assembly is withdrawn from the slurry bath and the cake is removed. The EAVF® is quoted as being best suited for the dewatering of ultrafine slurries (particle sizes typically less than 10 μm).

Cross-Flow–Electrofiltration

General References: Henry, Lawler, and Kuo, *Am. Inst. Chem. Eng. J.*, **23**(6), 851 (1977). Kuo, Ph.D. dissertation, West Virginia University, 1978.

Process Concept The application of a direct electric field of appropriate polarity when filtering should cause a net charged-particle migration away from the filter medium. This electrophoretic migration will prevent filter-cake formation and the subsequent reduction of filter performance. An additional benefit derived from the imposed electric field is an electroosmotic flux. The presence of this flux in the membrane and in any particulate accumulation may further enhance the filtration rate.

Cross-flow–electrofiltration (CF-EF) is the multifunctional separation process which combines the electrophoretic migration present in electrofiltration with the particle diffusion and radial-migration forces present in cross-flow filtration (CFF) (microfiltration includes cross-flow filtration as one mode of operation in "Membrane Separation Processes" which appears later in this section) in order to reduce further the formation of filter cake. Cross-flow–electrofiltration can even eliminate the formation of filter cake entirely. This process should find application in the filtration of suspensions when there are charged particles as well as a relatively low conductivity in the continuous phase. Low conductivity in the continuous phase is necessary in order to minimize the amount of electrical power necessary to sustain the electric field. Low-ionic-strength aqueous media and nonaqueous suspending media fulfill this requirement.

Cross-flow–electrofiltration has been investigated for both aqueous and nonaqueous suspending media by using both rectangular- and tubular-channel processing configurations (Fig. 22-27). Henry, Lawler, and Kuo (op. cit.), using a rectangular-channel system with a 0.6-μ-pore-size polycarbonate Nuclepore filtration membrane, investigated CF-EF for 2.5-μm kaolin-water and 0.5- to 2-μm oil-in-water emulsion systems. Kuo (op. cit.), using similar equipment, studied 5-μm kaolin-water, ~100-μm Cr_2O_3-water, and ~6-μm Al_2O_3-methanol and/or -butanol systems. For both studies electrical fields of 0 to 60 V/cm were used for aqueous systems, and to 5000 V/cm were used for nonaqueous systems. The studies covered a wide range of processing variables in order to gain a better understanding of CF-EF fundamentals. Lee, Gidaspow, and Wasan [*Ind. Eng. Chem. Fundam.*, **19**(2), 166 (1980)] studied CF-EF by using a porous stainless-steel tube (pore size = 5 μm) as the filtration medium. A platinum wire running down the center of the tube acted as one electrode, while the

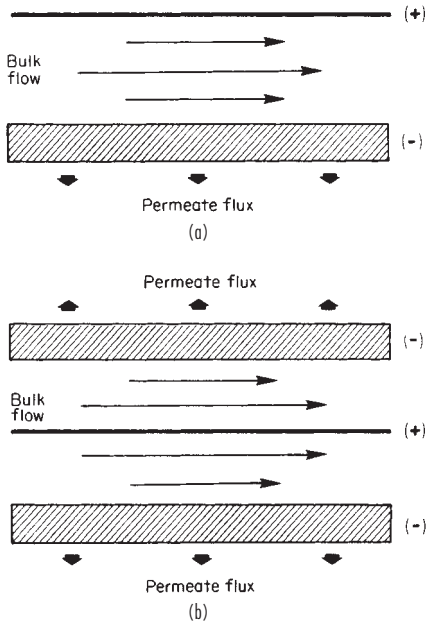


FIG. 22-27 Alternative electrode configurations for cross-flow–electrofiltration.

porous steel tube itself acted as the other electrode. Nonaqueous suspensions of 0.3- to 2-μm Al_2O_3-tetralin and a coal-derived liquid diluted with xylene and tetralin were studied. By operating with applied electric fields (1000 to 10,000 V/cm) above the critical voltage, clear particle-free filtrates were produced. It should be noted that the pore size of the stainless-steel filter medium (5 μm) was greater than the particle size of the suspended Al_2O_3 solids (0.3 to 2 μm). Cross-flow—electrofiltration has also been applied to biological systems. Brors, Kroner, and Deckwer [ECB6: Proc. 6th Eur. Cong. Biotech., 511 (1994)] separated malate dehydrogenase from the cellular debris of Baker's yeast using CF-EF. A two- to fivefold increase in the specific enzyme transport rate was reported when electric field strengths of 20 to 40 V/cm were used.

Theory Cross-flow–electrofiltration can theoretically be treated as if it were cross-flow filtration with superimposed electrical effects. These electrical effects include electroosmosis in the filter medium and cake and electrophoresis of the particles in the slurry. The addition of the applied electric field can, however, result in some qualitative differences in permeate-flux-parameter dependences.

The membrane resistance for CF-EF can be defined by specifying two permeate fluxes as

$$J_{om} = \Delta P / R_{om} \tag{22-29}$$

$$J_m = \Delta P / R_m \tag{22-30}$$

where J_{om} is the flux through the membrane in the absence of an electric field and any other resistance, m/s; J_m is the same flux in the presence of an electric field; and R_{om} is the membrane resistance in the absence of an electric field, $(N \cdot s)/m^3$. When electroosmotic effects do occur,

$$J_m = J_{om} + K_m E \tag{22-31}$$

where K_m is the electroosmotic coefficient of the membrane, $m^2/(V \cdot s)$; and E is the applied-electric-field strength, V/m. Equations (22-29), (22-30), and (22-31) can be combined and rearranged to give Eq. (22-32), the membrane resistance in the presence of an electric field.

$$R_m = \frac{R_{om}}{1 + \left(\dfrac{K_m E}{J_{om}}\right)} \tag{22-32}$$

Similarly, cake resistance can be represented as

$$R_c = \frac{R_{oc}}{1 + \left(\dfrac{K_c E}{J_{oc}}\right)} \tag{22-33}$$

where J_{oc} is the flux through the cake in the absence of an electric field or any other resistance, R_{oc} is the cake resistance in the absence of an electric field, and K_c is the electroosmotic coefficient of the cake. The cake resistance is not a constant but is dependent upon the cake thickness, which is in turn a function of the transmembrane pressure drop and electrical-field strength.

Particulate systems require the addition of the term $\mu_e E$ in order to account for the electrophoretic migration of the particle. The constant μ_e is the electrophoretic mobility of the particle, $m^2/(V \cdot s)$. For the case of the CF-EF, the film resistance R_f can be represented as

$$R_f = \frac{\Delta P}{k \ln\left(\dfrac{C_s}{C_b}\right) + U_r + \mu_e E} \tag{22-34}$$

The resistances, when incorporated into equations descriptive of cross-flow filtration, yield the general expression for the permeate flux for particulate suspensions in cross-flow-electrofiltration systems.

There are three distinct regimes of operation in CF-EF. These regimes (Fig. 22-28) are defined by the magnitude of the applied electric field with respect to the critical voltage E_c. The critical voltage is defined as the voltage at which the net particle migration velocity toward the filtration medium is zero. At the critical voltage, there is a balance between the electrical-migration and radial-migration velocities away from the filter and the velocity at which the particles are swept toward the filter by bulk flow. There is no diffusive transport at $E = E_c$ (Fig. 22-28*b*) because there is no gradient in the particle concentration normal to the filter surface. At field strengths below the critical voltage (Fig. 22-28*a*), all migration velocities occur in the same direction as in the cross-flow-filtration systems discussed earlier. At values of applied voltage above the critical voltage (Fig. 22-28*c*) qualitative differences are observed. In this case, the electrophoretic-migration velocity away from the filter medium is greater than the velocity caused by bulk flow toward the filtration medium. Particles concentrate away from the filter medium. This implies that particle concentration is lowest next to the filter medium (in actuality, a clear boundary layer has been observed). The influence of fluid shear still improves the transfer of particles down the concentration gradient, but in this case it is toward the filtration medium. When the particles are small and diffusive transport dominates radial migration, increasing the circulation velocity will decrease the permeate flux rate in this regime. When the particles are large and radial migration dominates, the increase in circulation velocity will still improve the filtration rate. These effects are illustrated qualitatively in Fig. 22-29*a*. The solid lines represent systems in which the particle diffusive effect dominates the radial-migration effect, while the dashed lines represent the inverse. Figure 22-29*b* illustrates the increase in filtration rate with increasing electric field strength. For field strengths $E > E_c$, increases in permeate flux rate are due only to electroosmosis in the filtration medium.

One potential difficulty with CF-EF is the electrodeposition of the particles at the electrode away from the filtration medium. This phenomenon, if allowed to persist, will result in performance decay of CF-EF with respect to maintenance of the electric field. Several approaches such as momentary reverses in polarity, protection of the electrode with a porous membrane or filter medium, and/or utilization of a high fluid shear rate can minimize electrodeposition.

Dielectrophoresis

GENERAL REFERENCES: Pohl, in Moore (ed.), *Electrostatics and Its Applications*, Wiley, New York, 1973, chap. 14 and chap. 15 (with Crane). Pohl, in Catsimpoolas (ed.), *Methods of Cell Separation*, vol. I, Plenum Press, New York, 1977, chap. 3. Pohl, *Dielectrophoresis: The Behavior of Matter in Nonuniform Electric Fields*, Cambridge, New York, 1978.

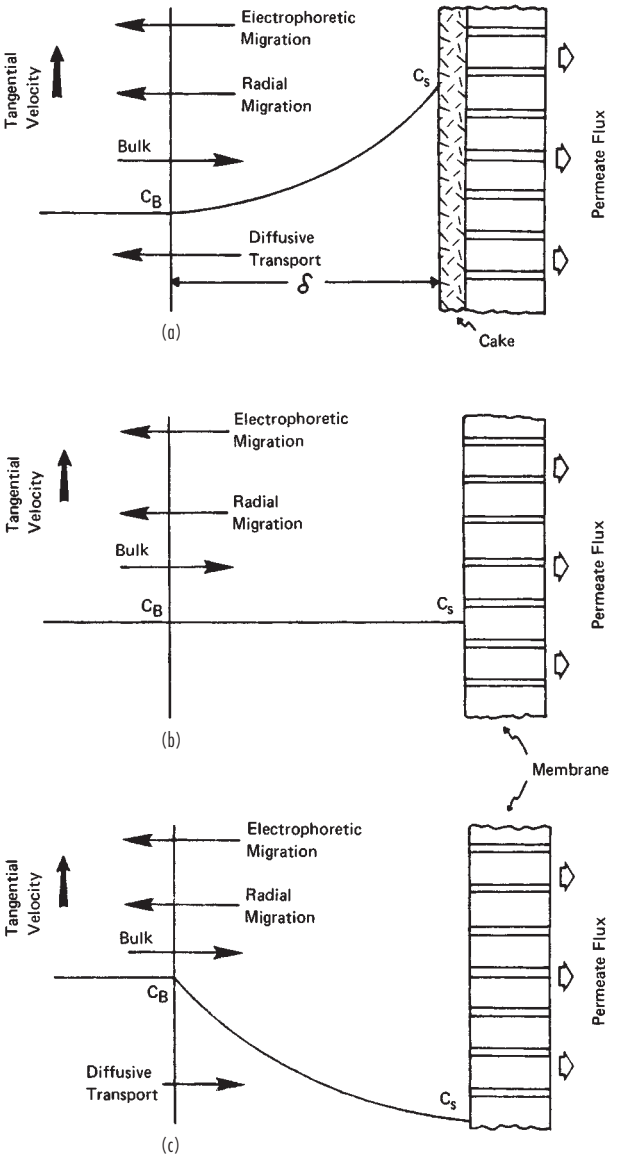


FIG. 22-28 Regimes of operation of cross-flow–electrofiltration: (*a*) voltage less than critical, (*b*) voltage equal to the critical voltage, (*c*) voltage greater than critical.

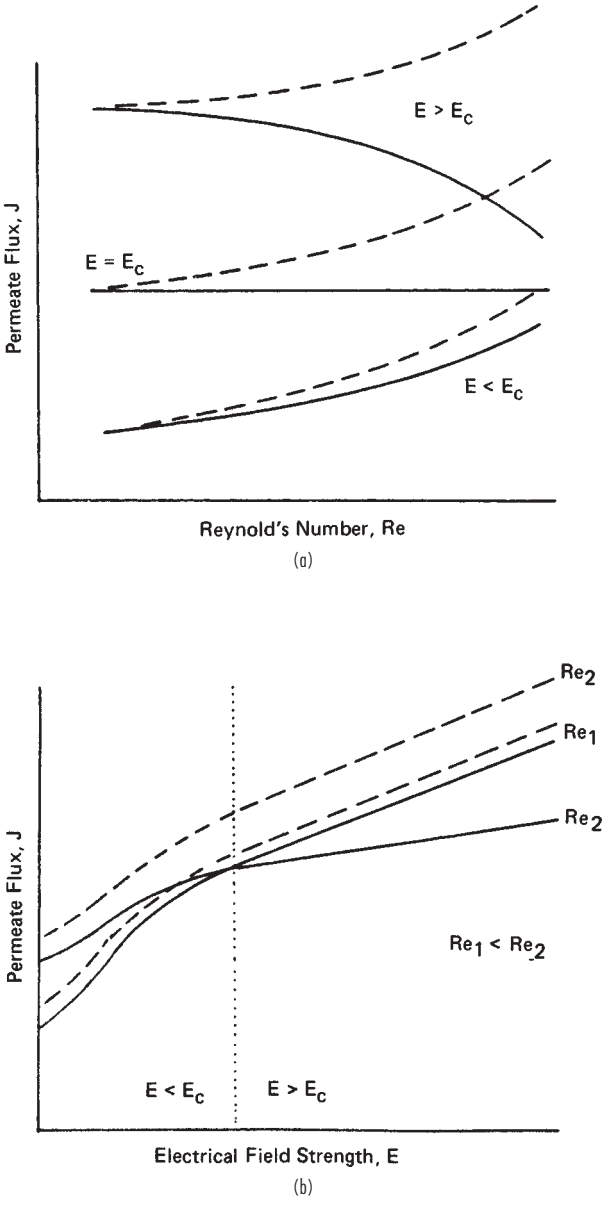


FIG. 22-29 Qualitative effects of Reynolds number and applied-electric-field strength on the filtration permeate flux *J*. Dashed lines indicate large particles (radial migration dominates); solid lines, small particles (particle diffusion dominates).

Introduction Dielectrophoresis (DEP) is defined as the motion of neutral, polarizable matter produced by a nonuniform electric (ac or dc) field. DEP should be distinguished from electrophoresis, which is the motion of charged particles in a uniform electric field (Fig. 22-30).

The DEP of numerous particle types has been studied, and many applications have been developed. Particles studied have included aerosols, glass, minerals, polymer molecules, living cells, and cell organelles. Applications developed include filtration, orientation, sorting or separation, characterization, and levitation and materials handling. Effects of DEP are easily exhibited, especially by large particles, and can be applied in many useful and desirable ways. DEP effects can, however, be observed on particles ranging in size even down to the molecular level in special cases. Since thermal effects tend to disrupt DEP with molecular-sized particles, they can be controlled only under special conditions such as in molecular beams.

Principle The principle of particle and cell separation, control, or characterization by the action of DEP lies in the fact that a net force can arise upon even neutral particles situated in a nonuniform electric field. The force can be thought of as rising from the imaginary two-step process of (1) induction or alignment of an electric dipole in a particle placed in an electric field followed by (2) unequal forces on the ends of that dipole. This arises from the fact that the force of an electric field upon a charge is equal to the amount of the charge and to the *local* field strength at that charge. Since the two (equal) charges of the (induced or oriented) dipole of the particle lie in unequal field strengths of the diverging field, a net force arises. If the particle is suspended in a fluid, then the polarizability of that medium enters, too. If, for example, the particle is more polarizable than the fluid, then the

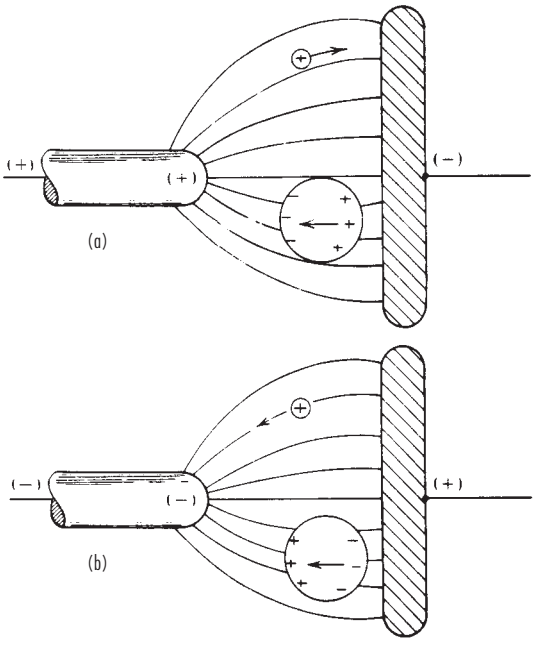


FIG. 22-30 Comparison of behaviors of neutral-charged bodies in an alternating nonuniform electric field. (*a*) Positively charged body moves toward negative electrode. Neutral body is polarized, then is attracted toward point where field is strongest. Since the two charge regions on the neutral body are equal in amount of charge but the force is proportional to the local field, a net force toward the region of more intense field results. (*b*) Positively charged body moves toward the negative electrode. Again, the neutral body is polarized, but it does not reverse direction although the field is reversed. It still moves toward the region of highest field intensity.

net force is such as to impel the particle to regions of greater field strength. Note that this statement implies that the effect is independent of the absolute sign of the field direction. This is found to be the case. Even rapidly alternating (ac) fields can be used to provide *unidirectional* motion of the suspended particles.

Formal Theory A small neutral particle at equilibrium in a static electric field experiences a net force due to DEP that can be written as $\mathbf{F} = (\mathbf{p} \cdot \nabla)\mathbf{E}$, where $\mathbf{p}$ is the dipole moment vector and $\mathbf{E}$ is the external electric field. If the particle is a simple dielectric and is isotropically, linearly, and homogeneously polarizable, then the dipole moment can be written as $\mathbf{p} = \alpha v\mathbf{E}$, where α is the (scalar) polarizability, v is the volume of the particle, and $\mathbf{E}$ is the external field. The force can then be written as:

$$\mathbf{F} = \alpha v(\mathbf{E} \cdot \nabla)\mathbf{E} = \tfrac{1}{2}\alpha v\nabla|\mathbf{E}|^2 \qquad (22\text{-}35)$$

This force equation can now be used to find the force in model systems such as that of an ideal dielectric sphere (relative dielectric constant K_2) in an ideal perfectly insulating dielectric fluid (relative dielectric constant K_1). The force can now be written as

$$\mathbf{F} = 2\pi a^3\varepsilon_0 K_1\left(\frac{K_2 - K_1}{K_2 + 2K_1}\right)\nabla|\mathbf{E}|^2 \qquad (22\text{-}36)$$

(ideal dielectric sphere in ideal fluid).

Heuristic Explanation As we can see from Fig. 22-31, the DEP response of *real* (as opposed to perfect insulator) particles with frequency can be rather complicated. We use a simple illustration to account for such a response. The force is proportional to the difference between the dielectric permittivities of the particle and the surrounding medium. Since a part of the polarization in real systems is thermally activated, there is a delayed response which shows as a phase lag between $\mathbf{D}$, the dielectric displacement, and $\mathbf{E}$, the electric-field intensity. To take this into account we may replace the simple (absolute) dielectric constant ε by the complex (absolute) dielectric

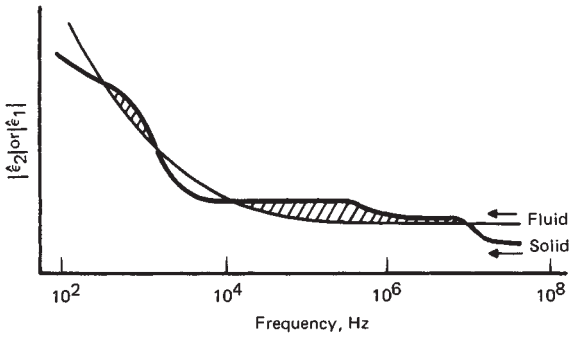


FIG. 22-31 A heuristic explanation of the dielectrophoretic-collection-rate (DCR)-frequency spectrum. The curves for the absolute values of the complex permittivities of the fluid medium and of the suspended particles are shown lying nearly, but not entirely, coincident over the frequency range of the applied electric field. When the permittivity (dielectric constant) of the particles exceeds that of the suspending medium, the collection, or "positive dielectrophoresis," occurs. In the frequency ranges in which the permittivity of the particles is less than that of the suspending medium no collection at the regions of higher field intensity occurs. Instead there is "negative dielectrophoresis," i.e., movement of the particles into regions of lower field intensity.

constant $\hat{\varepsilon} = \varepsilon' - i\varepsilon'' = \varepsilon' - i\sigma/w$, where ω is the angular frequency of the applied field. For treating spherical objects, for example, the replacement

$$F \propto \frac{\varepsilon_1(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2 + 2\varepsilon_1} \rightarrow \mathrm{Re}\left\{\frac{\hat{\varepsilon}_1^{\circ}(\hat{\varepsilon}_2 - \hat{\varepsilon}_1)}{\hat{\varepsilon}_2 + 2\hat{\varepsilon}_1}\right\} \qquad (22\text{-}37)$$

can be made, where $\hat{\varepsilon}^{\circ}$ is the complex conjugate of $\hat{\varepsilon}$.

With this force expression for real dielectrics, we can now explain the complicated DEP response with the help of Fig. 22-31.

A particle, such as a living cell, can be imagined as having a number of different frequency-dependent polarization mechanisms contributing to the total effective polarization of the particle $|\hat{\varepsilon}_2|$. The heavy curve in Fig. 22-31 shows that the various mechanisms in the particle drop out stepwise as the frequency increases. The light curve in Fig. 22-31 shows the polarization for a simple homogeneous liquid that forms the surrounding medium. This curve is a smooth function which becomes constant at high frequency. As the curves cross each other (and hence $|\varepsilon_2| = |\varepsilon_1|$), various responses occur. The particle can thus be attracted to the strongest field region, be repelled from that region, or experience no force depending on the frequency.

Limitations It is desirable to have an estimate for the smallest particle size that can be effectively influenced by DEP. To do this, we consider the force on a particle due to DEP and also due to the osmotic pressure. This latter diffusional force will randomize the particles and tend to destroy the control by DEP. Figure 22-32 shows a plot of these two forces, calculated for practical and representative conditions, as a function of particle radius. As we can see, the smallest particles that can be effectively handled by DEP appear to be in range of 0.01 to 0.1 μm (100 to 1000 Å).

Another limitation to be considered is the volume that the DEP force can affect. This factor can be controlled by the design of electrodes. As an example, consider electrodes of cylindrical geometry. A practical example of this would be a cylinder with a wire running down the middle to provide the two electrodes. The field in such a system is proportional to $1/r$. The DEP force is then $\mathbf{F}_{\mathrm{DEP}} \propto \nabla|E^2| \propto 1/r^3$, so that any differences in particle polarization might well be masked merely by positional differences in the force. At the outer cylinder the DEP force may even be too small to affect the particles appreciably. The most desirable electrode shape is one in which the force is independent of position within the nonuniform field. This "isomotive" electrode system is shown in Fig. 22-33.

Applications of Dielectrophoresis Over the past 20 years the use of DEP has grown rapidly to a point at which it is in use for biological, colloidal, and mineral materials studies and handling. The effects of nonuniform electric fields are used for handling particulate matter far more often than is usually recognized. This includes the

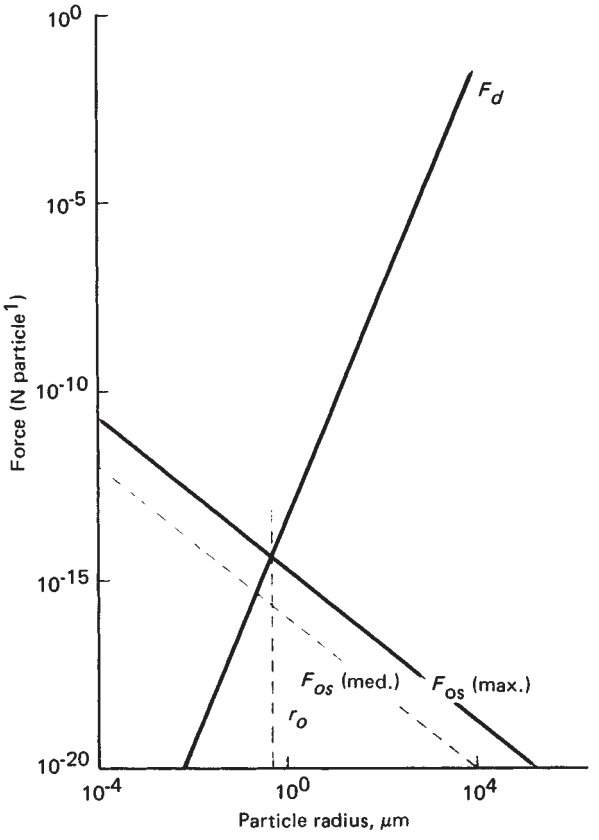


FIG. 22-32 Comparison of the dielectrophoretic (F_d) and osmotic (F_{os}) forces as functions of the particle size.

removal of particulate matter by "electrofiltration," the sorting of mixtures, or its converse, the act of mixing, as well as the coalescence of suspensions. In addition to these effects involving the translational motions of particles, some systems apply the orientational or torsional

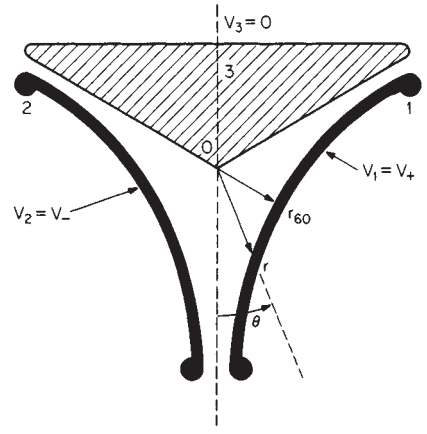


FIG. 22-33 A practical isomotive field geometry, showing r_{60}, the critical radius characterizing the isomotive electrodes. Electrode 3 is at ground potential, while electrodes 1 and 2 are at $V_1 = V_+$ and $V_2 = V_- = -V_+$ respectively. The inner faces of electrodes 1 and 2 follow $r = r_0\,[\sin(3\theta/2)]^{-2/3}$, while electrode 3 forms an angle of 120° about the midline.

forces available in nonuniform fields. One well-known example of the latter is the placing of "tip-up" grit on emery papers commercially. Xerography and many other imaging processes are examples of multibillion-dollar industries which depend upon DEP for their success.

A clear distinction between **electrophoresis** (field action on an object carrying excess free charges) and **dielectrophoresis** (field gradient action on neutral objects) must be borne in mind at all times.

A dielectrofilter [Lin and Benguigui, *Sep. Purif. Methods*, **10**(1), 53 (1981); Sisson et al., *Sep. Sci. Technol.*, **30**(7–9), 1421 (1995)] is a device which uses the action of an electric field to aid the filtration and removal of particulates from fluid media. A dielectrofilter can have a very obvious advantage over a mechanical filter in that it can remove particles which are much *smaller* than the flow channels in the filter. In contrast, the ideal mechanical filter must have all its passages smaller than the particles to be removed. The resultant flow resistance can be use-restrictive and energy-consuming unless a phenomenon such as dielectrofiltration is used.

Dielectrofiltration can (and often does) employ both electrophoresis and dielectrophoresis in its application. The precise physical process which dominates depends on a number of physical parameters of the system. Factors such as field intensity and frequency and the electrical conductivity and dielectric constants of the materials present determine this. Although these factors need constant attention for optimum operation of the dielectrofilter, this additional complication is often more than compensated for by the advantages of dielectrofiltration such as greater throughput and lesser sensitivity to viscosity problems, etc. To operate the dielectrofilter in the dominantly electrophoretic mode requires that excess free charges of one sign or the other reside on the particulate matter. The necessary charges can be those naturally present, as upon a charged sol; or they may need to be artificially implanted such as by passing the particles through a corona discharge. Dielectrofiltration by the corona-charging, electrophoresis-dominated Cottrell technique is now widely used.

To operate the dielectrofilter (dominantly dielectrophoretic mode), on the other hand, one must avoid the presence of free charge on the particles. If the particles can become charged during the operation, a cycle of alternate charging and discharging in which the particles dash to and from the electrodes can occur. This is most likely to occur if static or very low frequency fields are used. For this reason, corona and like effects may be troublesome and need often to be minimized. To be sure, the DEP force is proportional to the field applied [actually to $\nabla(E)^2$], but fields which are too intense can produce such troublesome charge injection. A compromise for optimal operation is necessary between having $\nabla(E)^2$ so low that DEP forces are insufficient for dependable operation, on the one hand, and having **E** so high that troublesome discharges (e.g., coronalike) interfere with dependable operation of the dielectrofilter. In insulative media such as air or hydrocarbon liquids, for example, one might prefer to operate with fields in the range of, say, 10 to 10,000 V/cm. In more conductive media such as water, acetone, or alcohol, for example, one would usually prefer rather lower fields in the range of 0.01 to 100 V/cm. The higher field ranges cited might become unsuitable if conductive sharp asperities are present.

Another factor of importance in dielectrofiltration is the need to have the DEP effect firmly operative upon *all* portions of the fluid passing through. Oversight of this factor is a most common cause of incomplete dielectrofiltration. Good dielectrofilter design will emphasize this crucial point. To put this numerically, let us consider the essential field factor for DEP force, namely $\nabla(\mathbf{E}_0)^2$. Near sharp points, e.g., **E,** the electric field varies with the radial distance r as $E \propto r^{-2}$; hence our DEP force factor will vary as $\nabla(E)^2 \propto r^{-5}$. In the neighborhood of sharp "line" sources such as at the edge of electrode plates, $E \propto r^{-1}$, hence, $\nabla(E)^2 \propto r^{-3}$. If, for instance, the distance is varied by a factor of 4 from the effective field source in these cases, the DEP force can be expected to weaken by a factor of 1024 or 64 respectively for the point source and the line source. The matter is even more keenly at issue when field-warping dielectrics (defined later) are used to effect maximal filtration. In this case the field-warping material is made to produce dipole fields as induced by the applied electric field. If we ask how the crucial factor, $\nabla(E)^2$, varies with distance away from such a dipole, we find that since the field E_d about a dipole varies

approximately as r^{-3}, then $\nabla(E)^2$ can be expected to vary as r^{-7}. It then becomes critically important that the particles to be removed from the passing fluid do, indeed, pass very close to the surface of the field-warping material, or it will not be effectively handled. Clearly, it would be difficult to maintain successfully uniform dielectrofiltration treatment of fluid passing through such wildly variant regions. The problems can be minimized by ensuring that all the elements of the passing fluid go closely by such field sources in the dielectrofilter. In practice this is done by constructing the dielectrofilter from an assembly of highly comminuted electrodes or else by a set of relatively simple and widely spaced metallic electrodes between which is set an assembly of more or less finely divided solid dielectric material having a complex permittivity different from that of the fluid to be treated. The solid dielectric (fibers, spheres, chunks) serves to produce field nonuniformities or **field warpings** to which the particles to be filtered are to be attracted. In treating fluids of low dielectric constant such as air or hydrocarbon fluids, one sees field-warping materials such as sintered ceramic balls, glass-wool matting, open-mesh polyurethane foam, alumina, chunks, or $BaTiO_3$ particles.

An example of a practical dielectrofilter which uses both of the features described, namely, sharp electrodes *and* dielectric field-warping filler materials, is that described in Fig. 22-34 [H. J. Hall and R. F. Brown, *Lubric. Eng.*, **22,** 488 (1966)]. It is intended for use with hydraulic fluids, fuel oils, lubricating oils, transformer oils, lubricants, and various refinery streams. Performance data are cited in Fig. 22-35. It must be remarked that in the opinion of Hall and Brown the action of the dielectrofilter was "electrostatic" and due to free charge on the particles dispersed in the liquids. It is the present authors' opinion, however, that both electrophoresis and dielectrophoresis are operative here but that the dominant mechanism is that of DEP, in which neutral particles are polarized and attracted to the regions of highest field intensity.

A second commercial example of dielectric filtration is the Gulftronic® separator [G. R. Fritsche, *Oil & Gas J.*, **75,** 73 (1977)] which was commercialized in the late 1970s by Gulf Science and Technology Company. Instead of using needle-point electrodes as shown in Fig. 22-34, the Gulftronic® separator relied on the use of a bed of glass beads to produce the field nonuniformities required for dielectric filtration. Either ac or dc electric fields could be used in this separator. The Gulftronic® separator has been used primarily to remove catalyst fines from FCC decant oils and has been reported to exhibit removal efficiencies in excess of 80 percent for this fine-particle separation problem.

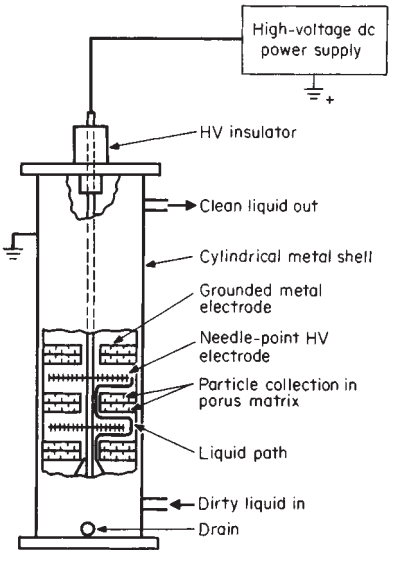


FIG. 22-34 Diagram illustrating the function of an electrostatic liquid cleaner.

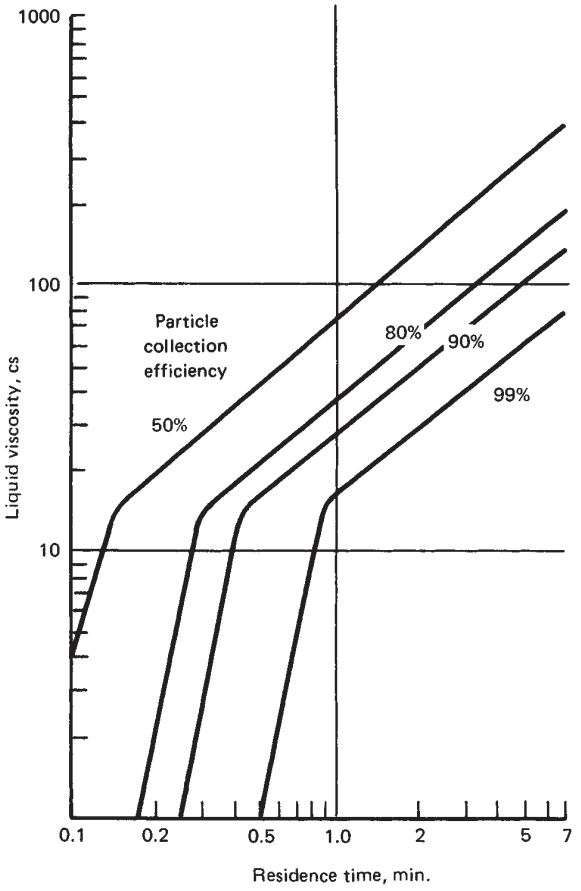


FIG. 22-35 Performance data for a typical high-efficiency electrostatic liquid cleaner.

Another example of the commercial use of DEP is in polymer clarification [A. N. Wennerberg, U.S. Patent 2,914,453, 1959; assignor to Standard Oil Co. (Indiana)]. Here, either ac or dc potentials were used while passing suspensions to be clarified through regions with an area-to-electrode-area ratio of 10:1 or 100:1 and with fields in the order of 10 kV/cm. Field warping by the presence of various solid dielectrics was observed to enhance filtration considerably, as expected for DEP. The filtration of molten or dissolved polymers to free them of objectionable quantities of catalyst residues, for example, was more effective if a solid dielectric material such as Attapulgus clay, silica gel, fuller's earth, alumina, or bauxite was present in the region between the electrodes. The effectiveness of percolation through such absorptive solids for removing color bodies is remarkably enhanced by the presence of an applied field. A given amount of clay is reported to remove from 4 to 10 times as much color as would be removed in the absence of DEP. Similar results are reported by Lin et al. [Lin, Yaniv, and Zimmels, *Proc. XIIIth Int. Miner. Process. Congr.*, Wrocław, Poland, 83–105 (1979)].

The instances cited were examples of the use of DEP to filter liquids. We now turn to the use of DEP to aid in dielectrofiltration of gases. Fielding et al. observe that the effectiveness of high-quality fiberglass air filters is dramatically improved by a factor of 10 or more by incorporating DEP in the operation. Extremely little current or power is required, and no detectable amounts of ozone or corona need result. The DEP force, once it has gathered the particles, continues to act on the particles already sitting on the filter medium, thereby improving adhesion and minimizing blowoff.

The degree by which the DEP increases the effectiveness of gas fil-

tration, or the dielectrophoretic augmentation factor (DAF), is definable. It is the ratio of the volumes of aerosol-laden gas which can be cleaned effectively by the filter with and without the voltage applied. For example, the application of 11 kV/cm gave a DAF of 30 for 1.0-μm-diameter dioctyl phthalate particles in air, implying that the penetration of the glass filter is reduced thirtyfold by the application of a field of 1100 kV/m. Similar results were obtained by using "standard" fly ash supplied by the Air Pollution Control Office of the U.S. Environmental Protection Agency. The data obtained for several aerosols tested are shown in Table 22-13 and in Fig. 22-36. The relation DAF = kV^2/v is observed to hold approximately for each aerosol. Here, the DEP augmentation factor DAF is observed to depend upon a constant K, a characteristic of the material, upon the square of the applied voltage, and upon the inverse of the volume flow rate v through the filter.

It is worth noting that in the case of the air filter described DEP serves as an augmenting rather than as an exclusive mechanism for the removal of particulate material. It is a unique feature of the dielectrophoretic gas filter that the DEP force is maximal when the particulates are at or on the fiber surface. This causes the deposits to be strongly retained by this particular filtration mechanism. It thus contrasts importantly with other types of gas filter in which the filtration mechanism no longer acts after the capture of the particle. In particular, in the case of the older electrostatic mechanisms involving only coulombic attraction, a simple charge alternation on the particle, such as caused by normal conduction, often evokes disruption of the filter operation because of particle repulsion from the contacting electrode. On the other hand, ordinary mechanical filtration depends upon the action of adventitious particle trapping or upon van der Waals forces, etc., to hold the particles. The high efficiency possible with electrofilters suggests their wider use.

TABLE 22-13 Dielectrophoretic Augmentation of Filtration of a Liquid Aerosol*

Air speed, cm/s	DAF at 2 kV	3.5 kV	5 kV	7 kV
0.3-μm-diameter dioctyl phthalate aerosol				
3	8	19	95	330
6	3	13	39	120
9	3	11	28	100
15	2	6	13	42
20	2	5	9	27
28	2	4	6	14
39	2	3	4	9
50	1	2	3	6
1.0-μm-diameter dioctyl phthalate aerosol				
3	30	110	300	1100
6	6	3	95	360
9	4	18	50	170
15	3	10	20	50
20	2	6	13	35
28	2	4	8	18
39	2	3	5	11
50	1	2	3	7
Fly-ash aerosol				
6	10	30	80	
10	8	30	80	
14	5	20	40	
20	4	10	30	70
35	3	7	10	20
45	1	2	6	
53	1	2	7	10

*Experimentally measured dielectrophoretic augmentation factor DAF as a function of air speed and applied voltage for a glass-fiber filter (HP-100, Farr Co.). Cf. Fielding, Thompson, Bogardus, and Clark, *Dielectrophoretic Filtration of Solid and Liquid Aerosol Particulates,* Prepr. 75-32.2, 68th ann. meet., Air Pollut. Control Assoc., Boston, June 1975.

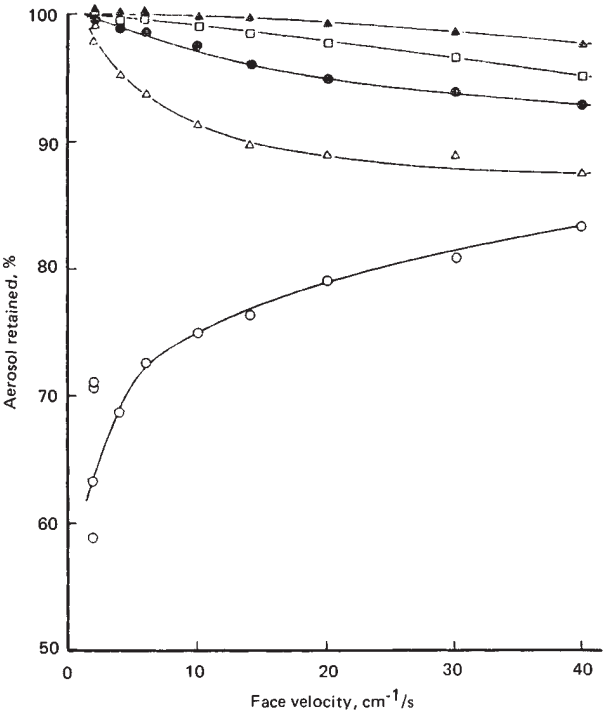


FIG. 22-36 Efficiency of an electrofilter as a function of gas flow rate at 5 different voltages. Experimental materials: 1-μm aerosol of dioctyl phthalate; glass-fiber filter. Symbols: ○, no voltage applied; Δ, 2 kV; ●, 3.5 kV; □, 5 kV; ▲, 7 kV. (*After Fielting et al.,* Dielectrophoretic Filtration of Solid and Liquid Aerosol Particulates, *Prepr. 75-32.2, 68th ann. meet., Air Pollut. Control Assoc., Boston, June 1975.*)

SURFACE-BASED SOLID-LIQUID SEPARATIONS INVOLVING A SECOND LIQUID PHASE

General References: Fuerstenau, "Fine Particle Flotation," in Somasundaran (ed.), *Fine Particles Processing,* vol. 1, American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1980. Henry, Prudich, and Lau, *Colloids Surf.,* **1,** 335 (1980). Henry, Prudich, and Vaidyanathan, *Sep. Purif. Methods,* **8**(2), 31 (1979). Jacques, Hovarongkura, and Henry, *Am. Inst. Chem. Eng. J.,* **25**(1), 160 (1979). Stratton-Crawley, "Oil Flotation: Two Liquid Flotation Techniques," in Somasundaran and Arbiter (eds.), *Beneficiation of Mineral Fines,* American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1979.

Process Concept Three potential surface-based regimes of separation exist when a second, immiscible liquid phase is added to another, solids-containing liquid in order to effect the removal of solids. These regimes (Fig. 22-37) are:

1. Distribution of the solids into the bulk second liquid phase
2. Collection of the solids at the liquid-liquid interface
3. Bridging or clumping of the solids by the added fluid in order to form an agglomerate followed by settling or filtration

These separation techniques should find particular application in systems containing fine particles. The surface chemical differences involved among these separation regimes are only a matter of degree; i.e., all three regimes require the wetting of the solid by the second liquid phase. The addition of a surface-active agent is sometimes needed in order to achieve the required solids wettability. In spite of this similarity, applied processing (equipment configuration, operating conditions, etc.) can vary widely. Collection at the interface would normally be treated as a flotation process (see also Sec. 22: "Adsorptive-Bubble Separation Methods"; and Sec. 19: "Flotation"), distribu-

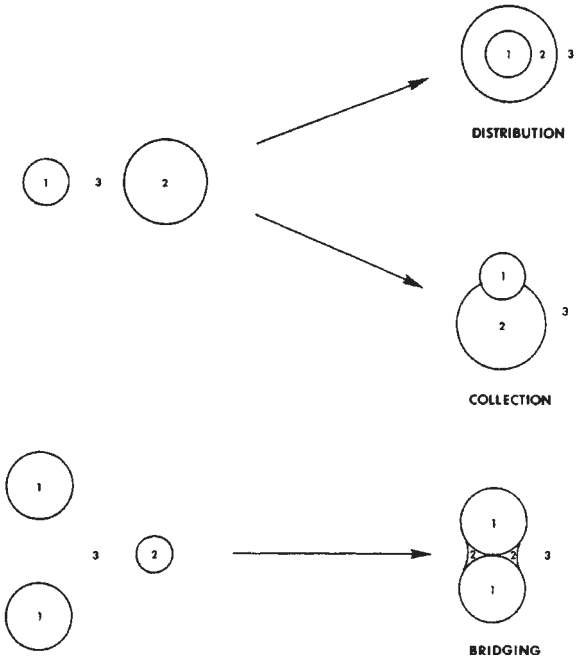


FIG. 22-37 Regimes of separation in a liquid-solid-liquid system. Phase 1 = particle; phase 2 = liquid (dispersed); phase 3 = liquid (continuous).

tion to the bulk liquid as a liquid-liquid extraction analog, and particle bridging as a settling (sedimentation) or filtration process.

Even though surface-property-based liquid-solid-liquid separation techniques have yet to be widely used in significant industrial applications, several studies which demonstrate their effectiveness have appeared in literature.

Albertsson (*Partition of Cell Particles and Macromolecules,* 3d ed., Wiley, New York, 1986) has extensively used particle distribution to fractionate mixtures of biological products. In order to demonstrate the versatility of particle distribution, he has cited the example shown in Table 22-14. The feed mixture consisted of polystyrene particles, red blood cells, starch, and cellulose. Liquid-liquid particle distribution has also been studied by using mineral-matter particles (average diameter = 5.5 μm) extracted from a coal liquid as the solid in a xylene-water system [Prudich and Henry, *Am. Inst. Chem. Eng. J.*, **24**(5), 788 (1978)]. By using surface-active agents in order to enhance the water wettability of the solid particles, recoveries of better than 95 percent of the particles to the water phase were observed. All particles remained in the xylene when no surfactant was added.

Particle collection at a liquid-liquid interface is a particularly favorable separation process when applied to fine-particle systems. Advantages of this type of processing include:

- Decreased liquid-liquid interfacial tension (when compared with a gas-liquid system) results in higher liquid-liquid interfacial areas, which favor solid-particle droplet collisions.
- Liquid-solid interactions due to long-range intermolecular forces are much larger than are gas-solid interactions. This means that it is easier to collect fine particles at a liquid-liquid interface than at a gas-liquid interface.
- The increased momentum of liquid droplets (when compared with gas) should favor solid-particle collection.

Fuerstenau [Lai and Fuerstenau, *Trans. Am. Inst. Min. Metall. Pet. Eng.,* **241,** 549 (1968); Raghavan and Fuerstenau, *Am. Inst. Chem. Eng.* Symp. Ser., **71**(150), 59 (1975)] has studied this process with respect to the removal of alumina particles (0.1 μm) and hematite particles (0.2 μm) from an aqueous solution by using isooctane. The use of isooctane as the collecting phase for the hematite particles resulted in an increase in particle recovery of about 50 percent over that measured when air was used as the collecting phase under the same conditions. The effect of the wettability of the solid particles (as measured by the three-phase contact angle) on the recovery of hematite in the water-isooctane system is shown in Fig. 22-38. This behavior is typical of particle collection. Particle collection at an oil-water interface has also been studied with respect to particle removal from a coal liquid. Particle removals averaging about 80 percent have been observed when water is used as the collecting phase (Lau, master's thesis, West Virginia University, 1979). Surfactant addition was necessary in order to control the wettability of the solids.

Particle bridging has been chiefly investigated with respect to spherical agglomeration. Spherical agglomeration involves the collecting or transferring of the fine particles from suspension in a liquid phase into spherical aggregates held together by a second liquid phase. The aggregates are then removed from the slurry by filtration or settling. Like the other liquid-solid-liquid separation techniques, the solid must be wet by the second liquid phase. The spherical agglomeration process has resulted in the development of a pilot unit called the Shell Pelletizing Separator [Zuiderweg and Van Lookeren Campagne, *Chem. Eng.* (*London*), **220,** CE223 (1968)]. A detailed discussion of spherical agglomeration can be found in Sec. 20: "Size Enlargement."

The ability to determine in advance which of the separation regimes is most advantageous for a given liquid-solid-liquid system would be desirable. No set of criteria with which to make this determination presently exists. Work has been done with respect to the identification of system parameters which make these processes technically feasible. The results of these studies can be used to guide the selection of the second liquid phase as well as to suggest approximate operating conditions (dispersed-liquid droplet size, degree and type of mixing, surface-active-chemical addition, etc.).

TABLE 22-14 Separations of Particles between Two Phases

System	Top phase	Bottom phase
Polyethylene glycol / salt	Polystyrene	All others
PEG / Dextran; 20,000 MW	Algae	All others
PEG / Dextran; 200,000 MW	Red cells	All others
Methyl cellulose / Dextran	Cellulose particles	Starch

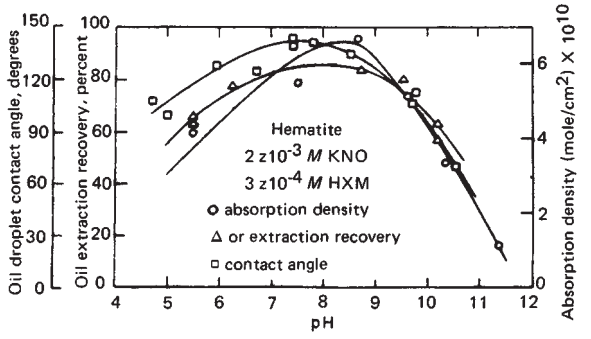


FIG. 22-38 The variation of adsorption density, oil-droplet contact angle, and oil-extraction recovery of hematite as a function of pH. To convert gram-moles per square centimeter to pound-moles per square foot, multiply by 2.048. [*From Raghavan and Fuerstenau,* Am. Inst. Chem. Eng. Symp. Ser., ***71****(150), 59 (1975).*]

Theory Theoretical analyses of spherical particles suspended in a planar liquid-liquid interface have appeared in literature for some time, the most commonly presented forms being those of a free energy and/or force balance made in the absence of all external body forces. These analyses are generally used to define the boundary criteria for the shift between the collection and distribution regimes, the bridging regime not being considered. This type of analysis shows that for a spherical particle possessing a three-phase contact angle between 0 and 180°, as measured through the receiving or collecting phase, collection at the interface is favored over residence in either bulk phase. These equations are summarized, using a derivation of Young's equation, as

$$\frac{\gamma_{s2} - \gamma_{s1}}{\gamma_{12}} > 1 \text{ particles wet to phase 1} \qquad (22\text{-}38)$$

$$\frac{\gamma_{s2} - \gamma_{s1}}{\gamma_{12}} < -1 \text{ particles wet to phase 2} \qquad (22\text{-}39)$$

$$\left|\frac{\gamma_{s2} - \gamma_{s1}}{\gamma_{12}}\right| \le 1 \text{ particle at interface} \qquad (22\text{-}40)$$

where γ_{ij} is the surface tension between phases i and j, N/m (dyn/cm); s indicates the solid phase; and subscripts 1 and 2 indicate the two liquid phases.

Several additional studies [Winitzer, *Sep. Sci.,* **8**(1), 45 (1973); ibid., **8**(6), 647 (1973); Maru, Wasan, and Kintner, *Chem. Eng. Sci.,* **26,** 1615 (1971); and Rapacchietta and Neumann, *J. Colloid Interface Sci.,* **59**(3), 555 (1977)] which include body forces such as gravitational acceleration and buoyancy have been made. A typical example of a force balance describing such a system (Fig. 22-39) is summarized in Eq. (22-41).

$$[(\gamma_{s1} - \gamma_{s2})\cos\delta + \gamma_{12}\cos B]L = g[V_{\text{total}}\rho_s - V_1\rho_1 - V_2\rho_2] \qquad (22\text{-}41)$$

where V_1 is the volume of the particle in fluid phase 1, V_2 is the volume in fluid phase 2, L is the particle circumference at the interface between the two liquid phases, ρ_i is the density of phase i, and g is the gravitational constant. The left-hand side of the equation represents the surface forces acting on the solid particle, while the right-hand side includes the gravitational and buoyancy forces. This example illustrates the fact that body forces can have a significant effect on system behavior. The solid-particle size as well as the densities of the solid and both liquid phases are introduced as important system parameters.

A study has also been performed for particle distribution for cases in which the radii of curvature of the solid and the liquid-liquid interface are of the same order of magnitude [Jacques, Hovarongkura, and Henry, *Am. Inst. Chem. Eng. J.,* **25**(1), 160 (1979)]. Differences between the final and initial surface free energies are used to analyze this system. Body forces are neglected. Results (Fig. 22-40) demonstrate that n, the ratio of the particle radius to the liquid-liquid-interface radius, is an important system parameter. Distribution of the particle from one phase to the other is favored over continued residence in the original phase when the free-energy difference is negative. For a solid particle of a given size, these results show that as the second-phase droplet size decreases, the contact angle required in order to effect distribution decreases (the required wettability of the solid by the second phase increases). The case of particle collection at a curved liquid-liquid interface has also been studied in a similar manner [Smith and Van de Ven, *Colloids Surf.,* **2,** 387 (1981)]. This study shows that collection is preferred over distribution for any n in systems without external body forces when the contact angle lies between 0 and 180°.

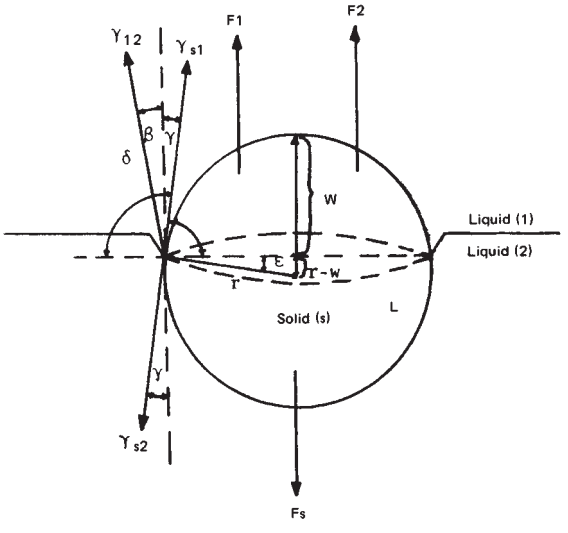


FIG. 22-39 Solid sphere suspended at the liquid-liquid interface. F_1 and F_2 are buoyancy forces; F_S is gravity. [*From Winitzer,* Sep. Sci., *8(1), 45 (1973).*]

While thermodynamic-stability studies can be valuable in evaluating the technical feasibility of a process, they are presently inadequate in determining which separation regime will dominate a particular liquid-solid-liquid system. These analyses ignore important processing phenomena such as the mechanism of encounter of the dispersed-phase liquid with the solid particles, the strength of particle attachment, and the mixing-energy input necessary to effect the separation. No models of good predictive value which take all these variables into account have yet been offered. Until the effects of these and other system variables can be adequately understood, quantified, and combined into such a predictive model, no a priori method of performance prediction will be possible.

ADSORPTIVE-BUBBLE SEPARATION METHODS

GENERAL REFERENCES: Lemlich (ed.), *Adsorptive Bubble Separation Techniques,* Academic, New York, 1972. Carleson, "Adsorptive Bubble Separation Processes" in Scamehorn and Harwell (eds.), *Surfactant-Based Separation Processes,* Marcel Dekker, New York, 1989.

Principle The adsorptive-bubble separation methods, or adsubble methods for short [Lemlich, *Chem. Eng.* **73**(21), 7 (1966)], are based on the selective adsorption or attachment of material on the surfaces of gas bubbles passing through a solution or suspension. In most of the methods, the bubbles rise to form a foam or froth which carries the material off overhead. Thus the material (desirable or undesirable) is removed from the liquid, and not vice versa as in, say, filtration. Accordingly, the foaming methods appear to be particularly (although not exclusively) suited to the removal of small amounts of material from large volumes of liquid.

For any adsubble method, if the material to be removed (termed the **colligend**) is not itself surface-active, a suitable surfactant (termed the **collector**) may be added to unite with it and attach or adsorb it to the bubble surface so that it may be removed (Sebba, *Ion Flotation,* Elsevier, New York, 1962). The union between colligend and collector may be by chelation or other complex formation. Alternatively, a charged colligend may be removed through its attraction toward a collector of opposite charge.

Definitions and Classification Figure 22-41 outlines the most widely accepted classification of the various adsubble methods [Karger, Grieves, Lemlich, Rubin, and Sebba, *Sep. Sci.,* **2,** 401 (1967)]. It is based largely on actual usage of the terms by various workers, and so the definitions include some unavoidable inconsistencies and overlap.

Among the methods of foam separation, **foam fractionation** usually implies the removal of dissolved (or sometimes colloidal) material. The overflowing foam, after collapse, is called the *foamate.* The solid lines of Fig. 22-42 illustrate simple continuous foam fractionation. (Batch operation would be represented by omitting the feed and bottoms streams.)

On the other hand, **flotation** usually implies the removal of solid particulate material. Most important under the latter category is **ore flotation,** which is covered separately in Sec. 19.

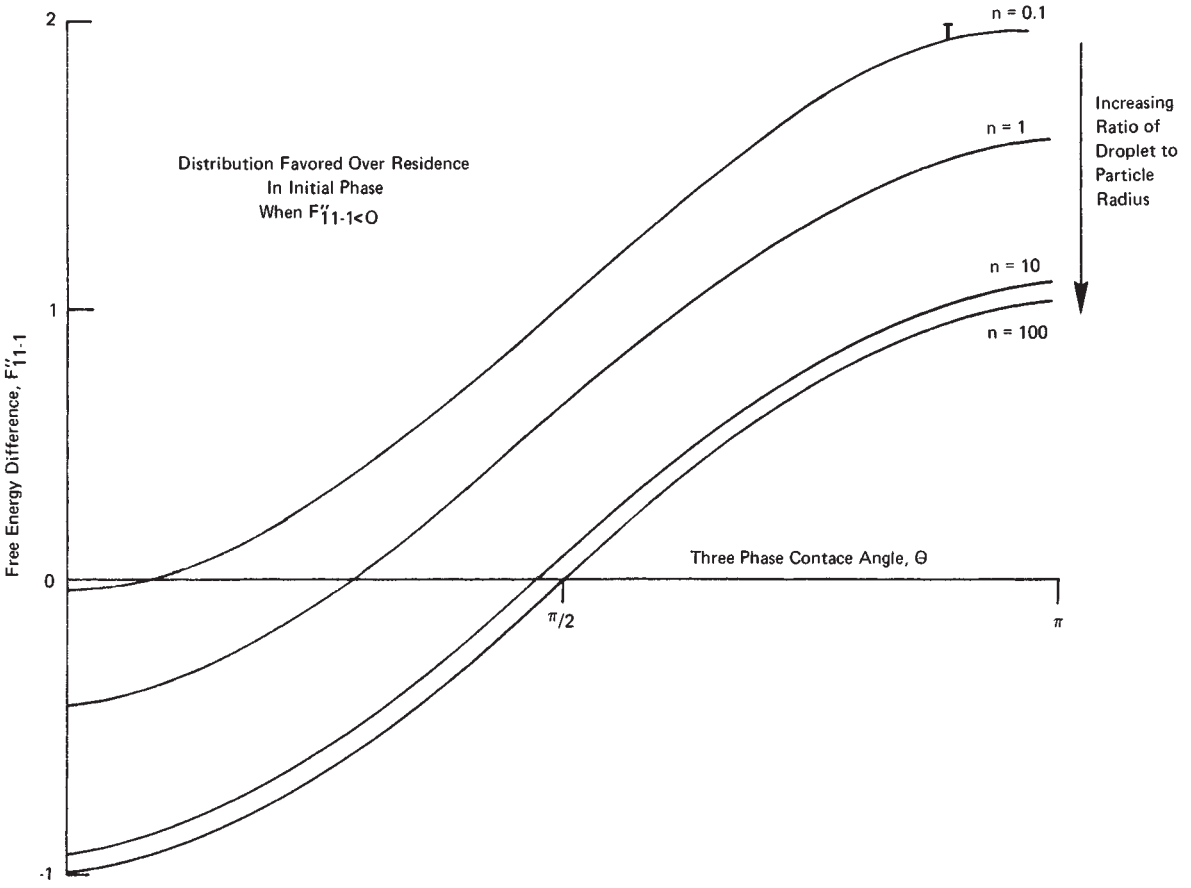


FIG. 22-40 Normalized free-energy difference between distributed (II) and nondistributed (I) states of the solid particles versus three-phase contact angle (collection at the interface is not considered). A negative free-energy difference implies that the distributed state is preferred over the nondistributed state. Note especially the significant effect of n, the ratio of the liquid droplet to solid-particle radius. [*From Jacques, Hovarongkura, and Henry,* Am. Inst. Chem. Eng. J., **25**(*1*), *160* (*1979*).]

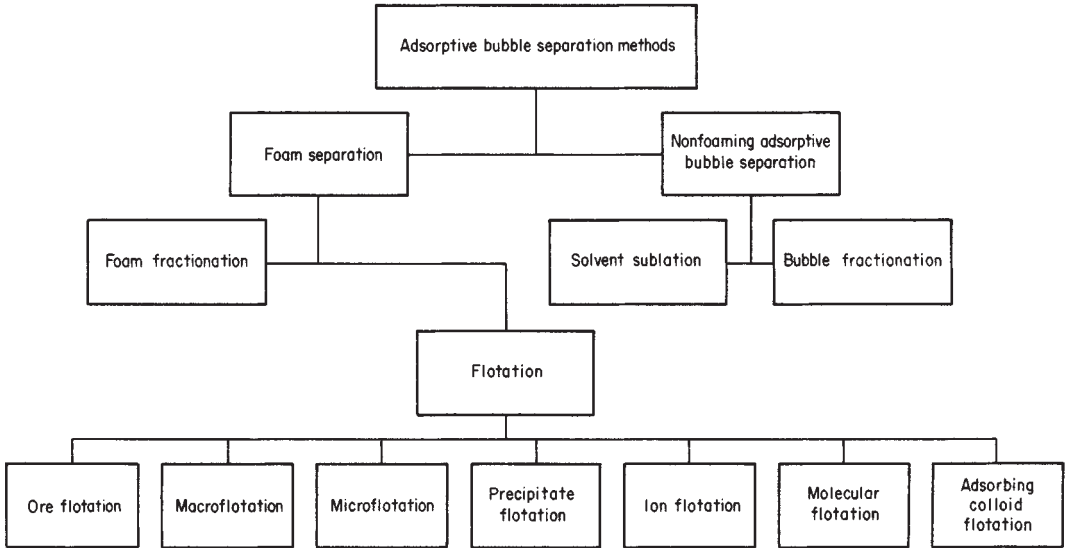


FIG. 22-41 Classification for the adsorptive-bubble separation methods.

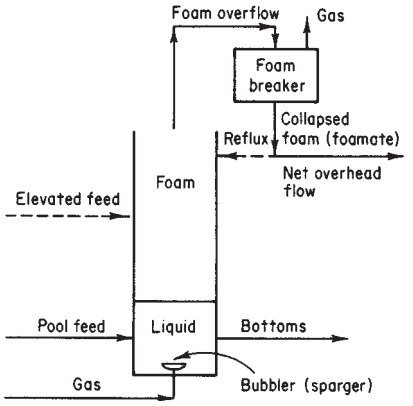


FIG. 22-42 Four alternative modes of continuous-flow operation with a foam-fractionation column: (1) The simple mode is illustrated by the solid lines. (2) Enriching operation employs the dashed reflux line. (3) In stripping operation, the elevated dashed feed line to the foam replaces the solid feed line to the pool. (4) For combined operation, reflux and elevated feed to the foam are both employed.

Also under the category of flotation are to be found **macroflotation,** which is the removal of macroscopic particles; **microflotation** (also called **colloid flotation**), which is the removal of microscopic particles, particularly colloids or microorganisms [Dognon and Dumontet, *Comptes Rendus,* **135,** 884 (1941)]; **molecular flotation,** which is the removal of surface-inactive molecules through the use of a collector (surfactant) which yields an insoluble product; **ion flotation,** which is the removal of surface-inactive ions via a collector which yields an insoluble product, especially a removable scum [Sebba, *Nature,* **184,** 1062 (1959)]; **adsorbing colloid flotation,** which is the removal of dissolved material in piggyback fashion by adsorption on colloidal particles; and **precipitate flotation,** in which a precipitate is removed by a collector which is not the precipitating agent [Baarson and Ray, "Precipitate Flotation," in Wadsworth and Davis (eds.), *Unit Processes in Hydrometallurgy,* Gordon and Breach, New York, 1964, p. 656]. The last definition has been narrowed to precipitate flotation of the first kind, the second kind requiring no separate collector at all [Mahne and Pinfold, *J. Appl. Chem.,* **18,** 52 (1968)].

A separation can sometimes be obtained even in the absence of any foam (or any floated floc or other surrogate). In **bubble fractionation** this is achieved simply by lengthening the bubbled pool to form a vertical column [Dorman and Lemlich, *Nature,* **207,** 145 (1965)]. The ascending bubbles then deposit their adsorbed or attached material at the top of the pool as they exit. This results in a concentration gradient which can serve as a basis for separation. Bubble fractionation can operate either alone or as a booster section below a foam fractionator, perhaps to raise the concentration up to the foaming threshold.

In **solvent sublation** an immiscible liquid is placed atop the main liquid to trap the material deposited by the bubbles as they exit (Sebba, *Ion Flotation,* Elsevier, New York, 1962). The upper liquid should dissolve or at least wet the material. With appropriate selectivity, the separation so achieved can sometimes be much greater than that with bubble fractionation alone.

The droplet analogs to the adsubble methods have been termed the **adsoplet methods** (from adsorptive droplet separation methods) [Lemlich, "Adsorptive Bubble Separation Methods," *Ind. Eng. Chem.,* **60**(10), 16 (1968)]. They are omitted from Fig. 22-41, since they involve adsorption or attachment at *liquid-liquid* interfaces. Among them are **emulsion fractionation** [Eldib, "Foam and Emulsion Fractionation," in Kobe and McKetta (eds.), *Advances in Petroleum Chemistry and Refining,* vol. 7, Interscience, New York, 1963, p. 66], which is the analog of foam fractionation; and **droplet fractionation** [Lemlich, loc. cit.; and Strain, *J. Phys. Chem.,* **57,** 638 (1953)], which is the analog of bubble fractionation. Similarly, the old beneficiation operation called bulk oil flotation (Gaudin, *Flotation,* 2d ed., McGraw-Hill, New York, 1957) is the analog of modern ore flotation. By and large, the adsoplet methods have not attracted the attention accorded to the adsubble methods.

Of all the adsubble methods, foam fractionation is the one for which chemical engineering theory is the most advanced. Fortunately, some of this theory also applies to other adsubble methods.

Adsorption The separation achieved depends in part on the selectivity of adsorption at the bubble surface. At equilibrium, the adsorption of dissolved material follows the Gibbs equation (Gibbs, *Collected Works,* Longmans Green, New York, 1928).

$$d\gamma = -\mathbf{R}T\Sigma\Gamma_i d\ln a_i \qquad (22\text{-}42)$$

Γ_i is the surface excess (Davies and Rideal, *Interfacial Phenomena,* 2d ed., Academic, New York, 1963). For most purposes, it is sufficient to view Γ_i as the concentration of adsorbed component i at the surface in units of, say (g·mol)/cm^2. **R** is the gas constant, T is the absolute temperature, γ is the surface tension, and a_i is the activity of component i. The minus sign shows that material which concentrates at the surface generally lowers the surface tension, and vice versa. This can sometimes be a guide in determining preliminarily what materials can be separated.

When applied to a nonionic surfactant in pure water at concentrations below the critical micelle concentration, Eq. (22-42) simplifies into Eq. (22-43)

$$\Gamma_s = -\frac{1}{\mathbf{R}T}\frac{d\gamma}{d\ln C_s} \qquad (22\text{-}43)$$

C is the concentration in the bulk, and subscript s refers to the surfactant. Under some conditions, Eq. (22-43) may apply to an ionic surfactant as well (Lemlich, loc. cit.).

The major surfactant in the foam may usually be considered to be present at the bubble surfaces in the form of an adsorbed monolayer with a substantially constant Γ_s, often of the order of 3×10^{-10} (g·mol)/cm^2, for a molecular weight of several hundred. On the other hand, trace materials follow the linear-adsorption isotherm $\Gamma_i = K_i C_i$ if their concentration is low enough. For a wider range of concentration a Langmuir or other type of isotherm may be applicable (Davies and Rideal, loc. cit.).

Factors Affecting Adsorption K_i for a colligend can be adversely affected (reduced) through an insufficiency of collector. It can also be reduced through an excess of collector, which competes for the available surface against the collector-colligend complex [Schnepf, Gaden, Mirocznik, and Schonfeld, *Chem. Eng. Prog.,* **55**(5), 42 (1959)].

Excess collector can also reduce the separation by forming micelles in the bulk which adsorb some of the colligend, thus keeping it from the surface. This effect of the micelles on K_i for the colligend is given theoretically [Lemlich, "Principles of Foam Fractionation," in Perry (ed.), *Progress in Separation and Purification,* vol. 1, Interscience, New York, 1968, chap. 1] by Eq. (22-44) [Lemlich (ed.), *Adsorptive Bubble Separation Techniques,* Academic, New York, 1972] if Γ_s is constant when $C_s > C_{sc}$:

$$\frac{1}{K_2} = \frac{1}{K_1} + \frac{C_s - C_{sc}}{\Gamma_s E} \qquad (22\text{-}44)$$

K_1 is K_i just below the collector's critical micelle concentration, C_{sc}. K_2 is K_i at some higher collector concentration, C_s. E is the relative effectiveness, in adsorbing colligend, of surface collector versus micellar collector. Generally, $E > 1$. Γ_s is the surface excess of collector. More about each K is available [Lemlich, "Adsubble Methods," in Li (ed.), *Recent Developments in Separation Science,* vol. 1, CRC Press, Cleveland, 1972, pp. 113–127; Jashnani and Lemlich, *Ind. Eng. Chem. Process Des. Dev.,* **12,** 312 (1973)].

The controlling effect of various ions can be expressed in terms of thermodynamic equilibria [Karger and DeVivo, *Sep. Sci.,* **3,** 393 1968)]. Similarities with ion exchange have been noted. The selectivity of counterionic adsorption increases with ionic charge and decreases with hydration number [Jorne and Rubin, *Sep. Sci.,* **4,** 313 (1969); and Kato and Nakamori, *J. Chem. Eng. Japan,* **9,** 378 (1976)].

By analogy with other separation processes, the relative distribution in multicomponent systems can be analyzed in terms of a selectivity coefficient $\alpha_{mn} = \Gamma_m C_n / \Gamma_n C_m$ [Rubin and Jorne, *Ind. Eng. Chem. Fundam.*, **8,** 474 (1969); *J. Colloid Interface Sci.*, **33,** 208 (1970)].

Operation in the Simple Mode If there is no concentration gradient within the liquid pool and if there is no coalescence within the rising foam, then the operation shown by the solid lines of Fig. 22-42 is truly in the simple mode, i.e., a single theoretical stage of separation. Equations (22-45) and (22-46) will then apply to the steady-flow operation.

$$C_Q = C_W + (GS\Gamma_W/Q) \tag{22-45}$$

$$C_W = C_F - (GS\Gamma_W/F) \tag{22-46}$$

C_F, C_W, and C_Q are the concentrations of the substance in question (which may be a colligend or a surfactant) in the feed stream, bottoms stream, and foamate (collapsed foam) respectively. G, F, and Q are the volumetric flow rates of gas, feed, and foamate respectively. Γ_W is the surface excess in equilibrium with C_W. S is the surface-to-volume ratio for a bubble. For a spherical bubble, $S = 6/d$, where d is the bubble diameter. For variation in bubble sizes, d should be taken as $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$, where n_i is the number of bubbles with diameter d_i in a representative region of foam.

Finding Γ Either Eq. (22-45) or Eq. (22-46) can be used to find the surface excess indirectly from experimental measurements. To assure a close approach to operation as a single theoretical stage, coalescence in the rising foam should be minimized by maintaining a proper gas rate and a low foam height [Brunner and Lemlich, *Ind. Eng. Chem. Fundam.* **2,** 297 (1963)]. These precautions apply particularly with Eq. (22-45).

For laboratory purposes it is sometimes convenient to recycle the foamate directly to the pool in a manner analogous to an equilibrium still. This eliminates the feed and bottoms streams and makes for a more reliable approach to steady-state operation. However, this recycling may not be advisable for colligend measurements in the presence of slowly dissociating collector micelles.

To avoid spurious effects in the laboratory, it is advisable to employ a prehumidified chemically inert gas.

Bubble Sizes Subject to certain errors (de Vries, *Foam Stability,* Rubber-Stichting, Delft, 1957), foam bubble diameters can be measured photographically. Some of these errors can be minimized by taking pains to generate bubbles of fairly uniform size, say, by using a bubbler with identical orifices or by just using a bubbler with a single orifice (gas rate permitting). Otherwise, a correction for planar statistical sampling bias in the foam should be incorporated with actual diameters [de Vries, op. cit.] or truncated diameters [Lemlich, *Chem. Eng. Commun.* **16,** 153 (1982)]. Also, size segregation can reduce mean mural bubble diameter by roughly half the standard deviation [Cheng and Lemlich, *Ind. Eng. Chem. Fundam.* **22,** 105 (1983)]. Bubble diameters can also be measured in the liquid pool, either photographically or indirectly via measurement of the gas flow rate and stroboscopic determination of bubble frequency [Leonard and Lemlich, *Am. Inst. Chem. Eng. J.*, **11,** 25 (1965)].

Bubble sizes at formation generally increase with surface tension and orifice diameter. Prediction of sizes in swarms from multiple orifices is difficult. In aqueous solutions of low surface tension, bubble diameters of the order of 1 mm are common. Bubbles produced by the more complicated techniques of pressure flotation or vacuum flotation are usually smaller, with diameters of the order of 0.1 mm or less.

Enriching and Stripping Unlike truly simple foam fractionation without significant changes in bubble diameter, coalescence in a foam column destroys some bubble surface and so releases adsorbed material to trickle down through the rising foam. This downflow constitutes internal reflux, which enriches the rising foam by countercurrent action. The result is a richer foamate, i.e., higher C_Q than that obtainable from the single theoretical stage of the corresponding simple mode. Significant coalescence is often present in rising foam, but the effect on bubble diameter and enrichment is frequently overlooked.

External reflux can be furnished by returning some of the externally broken foam to the top of the column. The concentrating effect of reflux, even for a substance which saturates the surface, has been verified [Lemlich and Lavi, *Science,* **134,** 191 (1961)].

Introducing the feed into the foam some distance above the pool makes for stripping operation. The resulting countercurrent flow in the foam further purifies the bottoms, i.e., lowers C_W.

Enriching, stripping, and combined operations are shown in Fig. 22-42.

Foam-Column Theory The counterflowing streams within the foam are viewed as consisting *effectively* of a descending stream of interstitial liquid (equal to zero for the simple mode) and an ascending stream of interstitial liquid plus bubble surface. (By considering this ascending surface as analogous to a vapor, the overall operation becomes analogous in a way to distillation *with entrainment.*)

An effective concentration $[\overline{C}]$ in the ascending stream at any level in the column is defined by Eq. (22-47):

$$\overline{C} = C + (GS\Gamma/U) \tag{22-47}$$

where U is the volumetric rate of interstitial liquid upflow, C is the concentration in this ascending liquid at that level, and Γ is the surface excess in equilibrium with C. Any effect of micelles should be included.

For simplicity, U can usually be equated to Q. An effective equilibrium curve can now be plotted from Eq. (22-47) in terms of $\overline{C}$ (or rather $\overline{C}°$) versus C.

Operating lines can be found in the usual way from material balances. The slope of each such line is $\Delta\overline{C}/\Delta C = L/U$, where L is the downflow rate in the particular column section and C is now the concentration in the descending stream.

The number of theoretical stages can then be found in one of the usual ways. Figure 22-43 illustrates a graphical calculation for a stripper.

Alternatively, the number of transfer units (NTU) in the foam based on, say, the ascending stream can be found from Eq. (22-48):

$$\text{NTU} = \int_{\overline{C}_W}^{C_Q} \frac{d\overline{C}}{\overline{C}° - \overline{C}} \tag{22-48}$$

$\overline{C}°$ is related to C by the effective equilibrium curve, and $\overline{C}°_W$ is similarly related to C_W. $\overline{C}$ is related to C by the operating line.

To illustrate this integration analytically, Eq. (22-48) becomes Eq. (22-49) for the case of a stripping column removing a colligend which is subject to the linear-equilibrium isotherm $\Gamma = KC$.

$$\text{NTU} = \frac{F}{GSK - W} \ln \frac{FW + F(GSK - W)C_F/C_W}{GSK(GSK + F - W)} \tag{22-49}$$

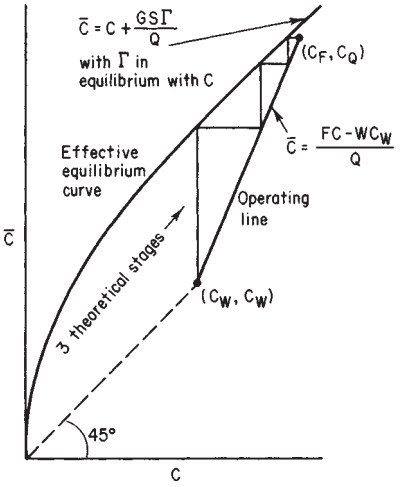


FIG. 22-43 Graphical determination of theoretical stages for a foam-fractionation stripping column.

As another illustration, Eq. (22-48) becomes Eq. (22-50) for an enriching column which is concentrating a surfactant with a constant Γ:

$$\text{NTU} = R \ln \frac{RGS\Gamma(F - D)}{(R + 1)GS\Gamma(F - D) - (R + 1)FD(C_D - C_F)} \qquad (22\text{-}50)$$

Unless the liquid pool is purposely lengthened vertically in order to give additional separation via bubble fractionation, it is usually taken to represent one theoretical stage. A bubbler submergence of 30 cm or so is usually ample for a solute with a molecular weight that does not exceed several hundred.

In a colligend stripper, it may be necessary to add some collector to the pool as well as the feed because the collector is also stripped off.

Limiting Equations If the height of a foam-fractionation column is increased sufficiently, a concentration pinch will develop between the counterflowing interstitial streams (Brunner and Lemlich, loc. cit.). For an enricher, the separation attained will then approach the predictions of Eq. (22-51) and, interestingly enough, Eq. (22-46).

$$C_D = C_W + (GS\Gamma_W/D) \qquad (22\text{-}51)$$

D is the volumetric rate at which net foamate (net overhead liquid product) is withdrawn. $D = Q/(R + 1)$. The concentration in the net foamate is C_D. In the usual case of total foam breakage (no dephlegmation), $C_D = C_Q$.

If the tall column is a stripper, the separation will approach that of Eqs. (22-52) and (22-53):

$$C_Q = C_F + (GS\Gamma_F/Q) \qquad (22\text{-}52)$$

$$C_W = C_F - (GS\Gamma_F/W) \qquad (22\text{-}53)$$

For a sufficiently tall combined column, the separation will approach that of Eqs. (22-54) and (22-53):

$$C_D = C_F + (GS\Gamma_F/D) \qquad (22\text{-}54)$$

The formation of micelles in the foam breaker does not affect the limiting equations because of the theoretically unlimited opportunity in a sufficiently tall column for their transfer from the reflux to the ascending stream [Lemlich, "Principles of Foam Fractionation," in Perry (ed.), *Progress in Separation and Purification,* vol. 1, Interscience, New York, 1968, chap. 1].

In practice, the performance of a well-operated foam column several feet tall may actually approximate the limiting equations, provided there is little channeling in the foam and provided that reflux is either absent or is present at a low ratio.

Column Operation To assure intimate contact between the counterflowing interstitial streams, the volume fraction of liquid in the foam should be kept below about 10 percent—and the lower the better. Also, rather uniform bubble sizes are desirable. The foam bubbles will thus pack together as blunted polyhedra rather than as spheres, and the suction in the capillaries (Plateau borders) so formed will promote good liquid distribution and contact. To allow for this desirable deviation from sphericity, $S = 6.3/d$ in the equations for enriching, stripping, and combined column operation [Lemlich, *Chem. Eng.,* **75**(27), 95 (1968); **76**(6), 5 (1969)]. Diameter d still refers to the sphere.

Visible channeling or significant deviations from plug flow of the foam should be avoided, if necessary by widening the column or lowering the gas and/or liquid rates. The superficial gas velocity should probably not exceed 1 or 2 cm/s. Under proper conditions, HTU values of several cm have been reported [Hastings, Ph.D. dissertation, Michigan State University, East Lansing, 1967; and Jashnani and Lemlich, *Ind. Eng. Chem. Process Des. Dev.,* **12,** 312 (1973)]. The foam column height equals NTU × HTU.

For columns that are wider than several centimeters, reflux and feed distributors should be used, particularly for wet foam [Haas and Johnson, *Am. Inst. Chem. Eng. J.,* **11,** 319 (1965)]. Liquid content within the foam can be monitored conductometrically [Chang and Lemlich, *J. Colloid Interface Sci.,* **73,** 224 (1980)]. See Fig. 22-44. Theoretically, as the limit $\mathscr{D} = K = 0$ is very closely approached, $\mathscr{D} = 3K$ [Lemlich, *J. Colloid Interface Sci.,* **64,** 107 (1978)].

Wet foam can be handled in a bubble-cap column (Wace and Banfield, *Chem. Process Eng.,* **47**(10), 70 (1966)] or in a sieve plate column [Aguayo and Lemlich, *Ind. Eng. Chem. Process Des. Dev.,* **13,** 153 (1974)]. Alternatively, individual short columns can be connected in countercurrent array [Banfield, Newson, and Alder, *Am. Inst. Chem. Eng. Symp. Ser.,* **1,** 3 (1965); Leonard and Blacyki, *Ind. Eng. Chem. Process Des. Dev.,* **17,** 358 (1978)].

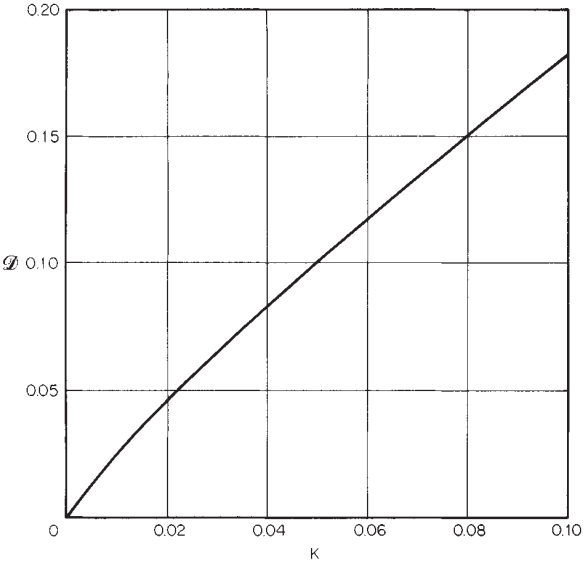


FIG. 22-44 Empirical relationship between $\mathscr{D}$, the volumetric fraction of liquid in common polydisperse foam, and K, the electrical conductivity of the foam divided by the electrical conductivity of the liquid. [*Chang and Lemlich,* J. Colloid Interface Sci., **73,** *224 (1980).*]

A high gas rate can be used to achieve maximum throughput in the simple mode (Wace, Alder, and Banfield, AERE-R5920, U.K. Atomic Energy Authority, 1968) because channeling is not a factor in that mode. A horizontal drainage section can be used overhead [Haas and Johnson, *Ind. Eng. Chem. Fundam.,* **6,** 225 (1967)]. The highly mobile dispersion produced by a very high gas rate is not a true foam but is rather a so-called **gas emulsion** [Bikerman, *Ind. Eng. Chem.,* **57**(1), 56 (1965)].

A very low gas rate in a column several feet tall with internal reflux can sometimes be used to effect difficult multicomponent separations in batch operation [Lemlich, "Principles of Foam Fractionation," in Perry (ed.), *Progress in Separation and Purification,* vol. 1, Interscience, New York, 1968, chap. 1].

The same end may be achieved by continuous operation at total external reflux with a small U bend in the reflux line for foamate holdup [Rubin and Melech, *Can. J. Chem. Eng.,* **50,** 748 (1972)].

The slowly rising foam in a tall column can be employed as the sorbent for continuous chromatographic separations [Talman and Rubin, *Sep. Sci.,* **11,** 509 (1976)]. Low gas rates are also employed in short columns to produce the scumlike froth of batch-operated ion flotation, microflotation, and precipitate flotation.

Foam Drainage and Overflow The rate of foam overflow on a gas-free basis (i.e., the total volumetric foamate rate Q) can be estimated from a detailed theory for foam drainage [Leonard and Lemlich, *Am. Inst. Chem. Eng. J.,* **11,** 18 (1965)]. From the resulting relationship for overflow [Fanlo and Lemlich, *Am. Inst. Chem. Eng. Symp. Ser.,* **9,** 75, 85 (1965)], Eq. (22-55) can be employed as a convenient approximation to the theory so as to avoid trial and error over the usual range of interest for foam of low liquid content ascending in plug flow:

$$\frac{Q}{G} = 22\left(\frac{v_G^3 \mu \mu_s^2}{g^3 \rho^3 d^8}\right)^{1/4} \qquad (22\text{-}55)$$

The superficial gas velocity v_g is G/A, where A is the horizontal

cross-sectional area of the empty vertical foam column. Also, g is the acceleration of gravity, ρ is the liquid density, μ is the ordinary liquid viscosity, and μ_s is the effective surface viscosity.

To account for inhomogeneity in bubble sizes, d in Eq. (22-55) should be taken as $\sqrt{\Sigma n_i d_i^3/\Sigma n_i d_i}$ and evaluated at the top of the vertical column if coalescence is significant in the rising foam. Note that this average d for overflow differs from that employed earlier for S. Also, see "Bubble Sizes" regarding the correction for planar statistical sampling bias and the presence of size segregation at a wall.

For theoretical reasons, Q determined from Eq. (22-55) should be multiplied by the factor $(1 + 3Q/G)$ to give a final Q. However, for foam of sufficiently low liquid content this multiplication can be omitted with little error.

The effective surface viscosity is best found by experiment with the system in question, followed by back calculation through Eq. (22-55). From the precursors to Eq. (22-55), such experiments have yielded values of μ_s on the order of 10^{-4} (dyn·s)/cm for common surfactants in water at room temperature, which agrees with independent measurements [Lemlich, *Chem. Eng. Sci.*, **23,** 932 (1968); and Shih and Lemlich, *Am. Inst. Chem. Eng. J.*, **13,** 751 (1967)]. However, the expected high μ_s for aqueous solutions of such skin-forming substances as saponin and albumin was not attained, perhaps because of their nonnewtonian surface behavior [Shih and Lemlich, *Ind. Eng. Chem. Fundam.*, **10,** 254 (1971); and Jashnani and Lemlich, *J. Colloid Interface Sci.*, **46,** 13 (1974)].

The drainage theory breaks down for columns with tortuous cross section, large slugs of gas, or heavy coalescence in the rising foam.

Foam Coalescence Coalescence is of two types. The first is the growth of the larger foam bubbles at the expense of the smaller bubbles due to interbubble gas diffusion, which results from the smaller bubbles having somewhat higher internal pressures (Adamson, *The Physical Chemistry of Surfaces,* 4th ed., Wiley, New York, 1982). Small bubbles can even disappear entirely. In principle, the rate at which this type of coalescence proceeds can be estimated [Ranadive and Lemlich, *J. Colloid Interface Sci.*, **70,** 392 (1979)].

The second type of coalescence arises from the rupture of films between adjacent bubbles [Vrij and Overbeek, *J. Am. Chem. Soc.*, **90,** 3074 (1968)]. Its rate appears to follow first-order reaction kinetics with respect to the number of bubbles [New, *Proc. 4th Int. Congr. Surf. Active Substances,* Brussels, 1964, **2,** 1167 (1967)] and to decrease with film thickness [Steiner, Hunkeler, and Hartland, *Trans. Inst. Chem. Eng.*, **55,** 153 (1977)]. Many factors are involved [Bikerman, *Foams,* Springer-Verlag, New York, 1973; and Akers (ed.), *Foams,* Academic, New York, 1976].

Both types of coalescence can be important in the foam separations characterized by low gas flow rate, such as batchwise ion flotation producing a scum-bearing froth of comparatively long residence time. On the other hand, with the relatively higher gas flow rate of foam fractionation, the residence time may be too short for the first type to be important, and *if* the foam is sufficiently stable, even the second type of coalescence may be unimportant.

Unlike the case for Eq. (22-55), when coalescence is significant, it is better to find S from d evaluated at the feed level for Eqs. (22-52) to (22-54) and at the pool surface for Eqs. (22-46) and (22-51).

Foam Breaking It is usually desirable to collapse the overflowing foam. This can be accomplished by chemical means (Bikerman, op. cit.) if external reflux is not employed or by thermal means [Kishimoto, *Kolloid Z.*, **192,** 66 (1963)] if degradation of the overhead product is not a factor.

Foam can also be broken with a rotating perforated basket [Lemlich, "Principles of Foam Fractionation," in Perry (ed.), *Progress in Separation and Purification,* vol. 1, Interscience, New York, 1968, chap. 1]. If the foamate is aqueous (as it usually is), the operation can be improved by discharging onto Teflon instead of glass [Haas and Johnson, *Am. Inst. Chem. Eng. J.*, **11,** 319 (1965)]. A turbine can be used to break foam [Ng, Mueller, and Walden, *Can. J. Chem. Eng.*, **55,** 439 (1977)]. Foam which is not overly stable has been broken by running foamate onto it [Brunner and Stephan, *Ind. Eng. Chem.*, **57**(5), 40 (1965)]. Foam can also be broken by sound or ultrasound, a rotating disk, and other means [Ohkawa, Sakagama, Sakai, Futai, and Takahara, *J. Ferment. Technol.*, **56,** 428, 532 (1978)].

If desired, dephlegmation (partial collapse of the foam to give reflux) can be accomplished by simply widening the top of the column, provided the foam is not too stable. Otherwise, one of the more positive methods of foam breaking can be employed to achieve dephlegmation.

Bubble Fractionation Figure 22-45 shows continuous bubble fractionation. This operation can be analyzed in a simplified way in terms of the adsorbed carry-up, which furthers the concentration gradient, and the dispersion in the liquid, which reduces the gradient [Lemlich, *Am. Inst. Chem. Eng. J.*, **12,** 802 (1966); **13,** 1017 (1967)].

To illustrate, consider the limiting case in which the feed stream and the two liquid takeoff streams of Fig. 22-45 are each zero, thus resulting in batch operation. At steady state the rate of adsorbed carry-up will equal the rate of downward dispersion, or $af\Gamma = \overline{D}AdC/dh$. Here a is the surface area of a bubble, f is the frequency of bubble formation. $\overline{D}$ is the dispersion (effective diffusion) coefficient based on the column cross-sectional area A, and C is the concentration at height h within the column.

There are several possible alternative relationships for Γ (Lemlich, op. cit.). For simplicity, consider $\Gamma = K'C$, where K' is not necessarily the same as the equilibrium constant K. Substituting and integrating from the boundary condition of $C = C_B$ at $h = 0$ yield

$$C/C_B = \exp(Jh) \tag{22-56}$$

C_B is the concentration at the bottom of the column, and parameter $J = K'af/\overline{D}A$. Combining Eq. (22-56) with a material balance against the solute in the initial charge of liquid gives

$$\frac{C}{C_i} = \frac{JH \exp(Jh)}{\exp(JH) - 1} \tag{22-57}$$

C_i is the concentration in the initial charge, and H is the total height of the column.

The foregoing approach has been extended to steady continuous flow as illustrated in Fig. 22-45 [Cannon and Lemlich, *Chem. Eng. Prog. Symp. Ser.*, **68**(124), 180 (1972); Bruin, Hudson, and Morgan, *Ind. Eng. Chem. Fundam.*, **11,** 175 (1972); and Wang, Granstrom, and Kown, *Environ. Lett.*, **3,** 251 (1972), **4,** 233 (1973), **5,** 71 (1973)]. The extension includes a rough method for estimating the optimum feed location as well as a very detailed analysis of column performance which takes into account the various local phenomena around each rising bubble (Cannon and Lemlich, op. cit.).

Uraizee and Narsimhan [*Sep. Sci. Technol.*, **30**(6), 847 (1995)] have provided a model for the continuous separation of proteins from dilute solutions. Although their work is focused on protein separation, the model should find general application to other separations.

In agreement with experiment [Shah and Lemlich, *Ind. Eng. Chem. Fundam.*, **9,** 350 (1970); and Garmendia, Perez, and Katz,

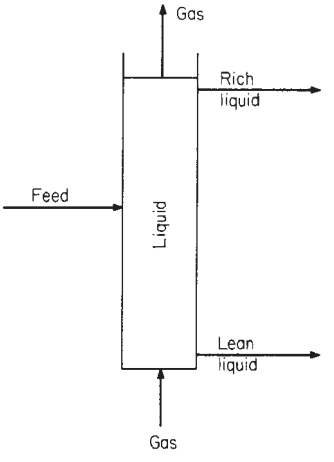


FIG. 22-45 Continuous bubble fractionation.

J. Chem. Educ., **50,** 864 (1973)], theory shows that the degree of separation that is obtained increases as the liquid column is made taller. But unfortunately it decreases as the column is made wider. In simple terms, the latter effect can be attributed to the increase in the dispersion coefficient as the column is widened.

In this last connection it is important that the column be aligned precisely vertically (Valdes-Krieg, King, and Sephton, *Am. Inst. Chem. Eng. J.,* **21,** 400 (1975)]. Otherwise, the bubbles with their dragged liquid will tend to rise up one side of the column, thus causing liquid to flow down the other side, and in this way largely destroy the concentration gradient. A vertical foam-fractionation column should also be carefully aligned to be plumb.

The escaping bubbles from the top of a bubble-fractionation column can carry off an appreciable quantity of adsorbed material in an aerosol of very fine film drops [various papers, *J. Geophys. Res., Oceans Atmos.,* **77**(27), (1972)]. If the residual solute is thus appreciably depleted, C_i in Eq. (22-57) should be replaced with the average residual concentration.

This carry-off of film drops, which may also occur with breaking foam, in certain cases can partially convert water pollution into air pollution. If such is the case, it may be desirable to recirculate the gas. Such recirculation is also indicated if hydrocarbon vapors or other volatiles are incorporated in the gas stream to improve adsorptive selectivity [Maas, *Sep. Sci.,* **4,** 457 (1969)].

A small amount of collector (surfactant) or other appropriate additive in the liquid may greatly increase adsorption (Shah and Lemlich, op. cit.). Column performance can also be improved by skimming the surface of the liquid pool or, when possible, by removing adsorbed solute in even a tenuous foam overflow. Alternatively, an immiscible liquid can be floated on top. Then the concentration gradient in the tall pool of main liquid, plus the trapping action of the immiscible layer above it, will yield a combination of bubble fractionation and solvent sublation.

Systems Separated Some of the various separations reported in the literature are listed in Rubin and Gaden, "Foam Separation," in Schoen (ed.), *New Chemical Engineering Separation Techniques,* Interscience, New York, 1962, chap. 5; Lemlich, *Ind. Eng. Chem.,* **60**(10), 16 (1968); Pushkarev, Egorov, and Khrustalev, *Clarification and Deactivation of Waste Waters by Frothing Flotation,* in Russian, Atomizdat, Moscow, 1969; Kuskin and Golman, *Flotation of Ions and Molecules,* in Russian, Nedra, Moscow, 1971; Lemlich (ed.), *Adsorptive Bubble Separation Techniques,* Academic, New York, 1972; Lemlich, "Adsubble Methods," in Li (ed.), *Recent Developments in Separation Science,* vol. 1, CRC Press, Cleveland, 1972, chap. 5; Grieves, *Chem. Eng. J.,* **9,** 93 (1975); Valdes-Krieg King, and Sephton, *Sep. Purif. Methods,* **6,** 221 (1977); Clarke and Wilson, *Foam Flotation,* Marcel Dekker, New York, 1983; and Wilson and Clarke, "Bubble and Foam Separations in Waste Treatment," in Rousseau (ed.), *Handbook of Separation Processes,* Wiley, New York, 1987.

Of the numerous separations reported, only a few can be listed here. Except for minerals beneficiation [ore flotation] which is covered in Sec. 21, the most important industrial applications are usually in the area of pollution control.

A pilot-sized foaming unit reduced the alkyl benzene sulfonate concentration of 500,000 gal of sewage per day to nearly 1 mg/L, using a G/F of 5 and producing a Q/F of no more than 0.03 [Brunner and Stephan, *Ind. Eng. Chem.,* **57**(5), 40 (1965); and Stephan, *Civ. Eng.,* **35**(9), 46 (1965)]. A full-scale unit handling over 45,420 m^3/day (12 million gal/day) performed nearly as well. The foam also carried off some other pollutants. However, with the widespread advent of biodegradable detergents, large-scale foam fractionation of municipal sewage has been discontinued.

Other plant-scale applications to pollution control include the flotation of suspended sewage particles by depressurizing so as to release dissolved air [Jenkins, Scherfig, and Eckhoff, "Applications of Adsorptive Bubble Separation Techniques to Wastewater Treatment," in Lemlich (ed.), *Adsorptive Bubble Separation Techniques,* Academic, New York, 1972, chap. 14; and Richter, *Internat. Chem. Eng.,* **16,** 614 (1976)]. Dissolved-air flotation is also employed in treating wastewater from pulp and paper mills [Coertze, *Prog. Water Technol.,* **10,** 449 (1978); and Severeid, *TAPPI* **62**(2), 61, 1979]. In addition, there is the flotation, with electrolytically released bubbles [Chambers and Cottrell, *Chem. Eng.,* **83**(16), 95 (1976)], of oily iron dust [Ellwood, *Chem. Eng.,* **75**(16), 82 (1968)] and of a variety of wastes from surface-treatment processes at the maintenance and overhaul base of an airline [Roth and Ferguson, *Desalination,* **23,** 49 (1977)].

Fats and, through the use of lignosulfonic acid, proteins can be flotated from the wastewaters of slaughterhouses and other food-processing installations [Hopwood, *Inst. Chem. Eng. Symp. Ser.,* **41,** M1 (1975)]. After further treatment, the floated sludge has been fed to swine.

A report of the recovery of protein from potato-juice wastewater by foaming [Weijenberg, Mulder, Drinkenberg, and Stemerding, *Ind. Eng. Chem. Process Des. Dev.,* **17,** 209 (1978)] is reminiscent of the classical recovery of protein from potato and sugar-beet juices [Ostwald and Siehr, *Kolloid Z.,* **79,** 11 (1937)]. The isoelectric pH is often a good choice for the foam fractionation of protein (Rubin and Gaden, loc. cit.). Adding a salt to lower solubility may also help. Additional applications of foam fractionation to the separation of protein have been reported by Uraizee and Narsimhan [*Enzyme Microb. Technol.* **12,** 232 (1990)].

With the addition of appropriate additives as needed, the flotation of refinery wastewaters reduced their oil content to less than 10 mg/L in pilot-plant operation [Steiner, Bennett, Mohler, and Clere, *Chem. Eng. Prog.,* **74**(12), 39 (1978)] and full-scale operation (Simonsen, *Hydrocarb. Process. Pet. Refiner,* **41**(5), 145, 1962]. Experiments with a cationic collector to remove oils reportedly confirmed theory [Angelidon, Keskavarz, Richardson, and Jameson, *Ind. Eng. Chem. Process Des. Dev.,* **16,** 436 (1977)].

Pilot-plant [Hyde, Miller, Packham, and Richards, *J. Am. Water Works Assoc.,* **69,** 369 (1977)] and full-scale [Ward, *Water Serv.,* **81,** 499 (1977)] flotation in the preparation of potable water is described.

Overflow at the rate of 2700 m^3 (713,000 gal) per day from a zinc-concentrate thickener is treated by ion flotation, precipitate flotation, and untrafine-particle flotation [Nagahama, *Can. Min. Metall. Bull.,* **67,** 79 (1974)]. In precipitate flotation only the surface of the particles need be coated with collector. Therefore, in principle less collector is required than for the equivalent removal of ions by foam fractionation or ion flotation.

By using an anionic collector and external reflux in a combined (enriching and stripping) column of 3.8-cm (1.5-in) diameter with a feed rate of 1.63 m/h [40 gal/(h·ft^2)] based on column cross section, D/F was reduced to 0.00027 with C_w/C_F for Sr^{2+} below 0.001 [Shonfeld and Kibbey, *Nucl. Appl.,* **3,** 353 (1967)]. Reports of the adsubble separation of 29 heavy metals, radioactive and otherwise, have been tabulated [Lemlich, "The Adsorptive Bubble Separation Techniques," in Sabadell (ed.), *Proc. Conf. Traces Heavy Met. Water,* 211–223, Princeton University, 1973, EPA 902/9-74-001, U.S. EPA, Reg. II, 1974). Some separation of ^{15}N from ^{14}N by foam fractionation has been reported [Hitchcock, Ph.D. dissertation, University of Missouri, Rolla, 1982].

The numerous separations reported in the literature include surfactants, inorganic ions, enzymes, other proteins, other organics, biological cells, and various other particles and substances. The scale of the systems ranges from the simple Crits test for the presence of surfactants in water, which has been shown to operate by virtue of transient foam fractionation [Lemlich, *J. Colloid Interface Sci.,* **37,** 497 (1971)], to the natural adsubble processes that occur on a grand scale in the ocean [Wallace and Duce, *Deep Sea Res.,* **25,** 827 (1978)]. For further information see the reviews cited earlier.

MEMBRANE SEPARATION PROCESSES

General References: Noble and Stern (eds.), *Membrane Separations Technology,* Elsevier, 1995. Howell, Sanchez, and Field, *Membranes in Bioprocessing,* Chapman & Hall, 1993. Ho and Sirkar (eds.), *Membrane Handbook,* Van Nostrand Reinhold, 1992. Mulder, *Basic Principles of Membrane Technology,* Kluwer Academic Publishers, 1992. Bhave, *Inorganic Membranes: Synthesis, Characteristics, and Applications,* Chapman & Hall, 1991. Baker, Cussler, Eykamp, Koros, Riley, and Strathmann, *Membrane Separation Systems,* U.S. Department of Energy, DOE/ER/30133-H1, 1990. Porter (ed.), *Handbook of Industrial Membrane Technology,* Noyes, 1990. Wankat, *Rate-Controlled Separations,* chapters 12 and 13, Elsevier, 1990. Rautenbach and Albrecht, *Membrane Processes,* Wiley, 1989. Mohr, Leeper, Engelgau, and Charboneau, *Membrane Applications and Research in Food Processing,* Noyes, 1989. Li and Strathmann, *Separation Technology,* United Engineering Trustees, 1988. Cheryan, *Ultrafiltration Handbook,* Technomic Publishing, Lancaster, PA, 1986. Speigler and Laird, *Principles of Desalination, 2d ed.,* Academic Press, 1980. Many membrane research papers are published in *J. Membrane Sci.,* Elsevier.

Topics Omitted from This Section In order to concentrate on the membrane processes of widest industrial interest, several are left out.

Dialysis and Hemodialysis Historically, dialysis has found some industrial use. Today, much of that is supplanted by ultrafiltration. Donan dialysis is treated briefly under electrodialysis. Hemodialysis is a huge application for membranes, and it dominates the membrane field in area produced and in monetary value. This medical application is omitted here.

An excellent description of the engineering side of both topics is provided by Kessler and Klein [in Ho and Sirkar (eds.), op. cit., pp. 163–216]. A comprehensive treatment of diffusion appears in: Von Halle and Shachter, "Diffusional Separation Methods," in *Encyclopedia of Chemical Technology,* pp. 149–203, Wiley, 1993.

Facilitated Transport Transport by a reactive phase through a membrane is promising but problematic. Way and Noble [in Ho and Sirkar (eds.), op. cit., pp. 833–866] have a description and a complete bibliography.

Liquid Membranes Several types of liquid membranes exist: molten salt, emulsion, immobilized/supported, and hollow-fiber-contained liquid membranes. Araki and Tsukube (*Liquid Membranes: Chemical Applications,* CRC Press, 1990) and Sec. IX and Chap. 42 in Ho and Sirkar (eds.) (op. cit., pp. 724, 764–808) contain detailed information and extensive bibliographies.

Catalytic Membranes Falconer, Noble, and Sperry (Chap. 14—"Catalytic Membrane Reactors" in Noble and Stern, op. cit., p. 669–712) give a detailed review and an extensive bibliography. Additional information can be found in a work by Tsotsis et al. ["Catalytic Membrane Reactors," pp. 471–551, in Becker and Pereira (eds.), *Computer-Aided Design of Catalysts,* Dekker, 1993].

BACKGROUND AND DEFINITIONS

This section describes the use of separation processes which utilize membranes. Placement in this chapter is in recognition of the recent ascendency of industrial-scale membrane-based separations, but it also reflects the view that within a decade, many of these separation processes will be mainstream unit operations. Some approach that status already. Figure 22-46 shows the relative size of things important in membrane separations.

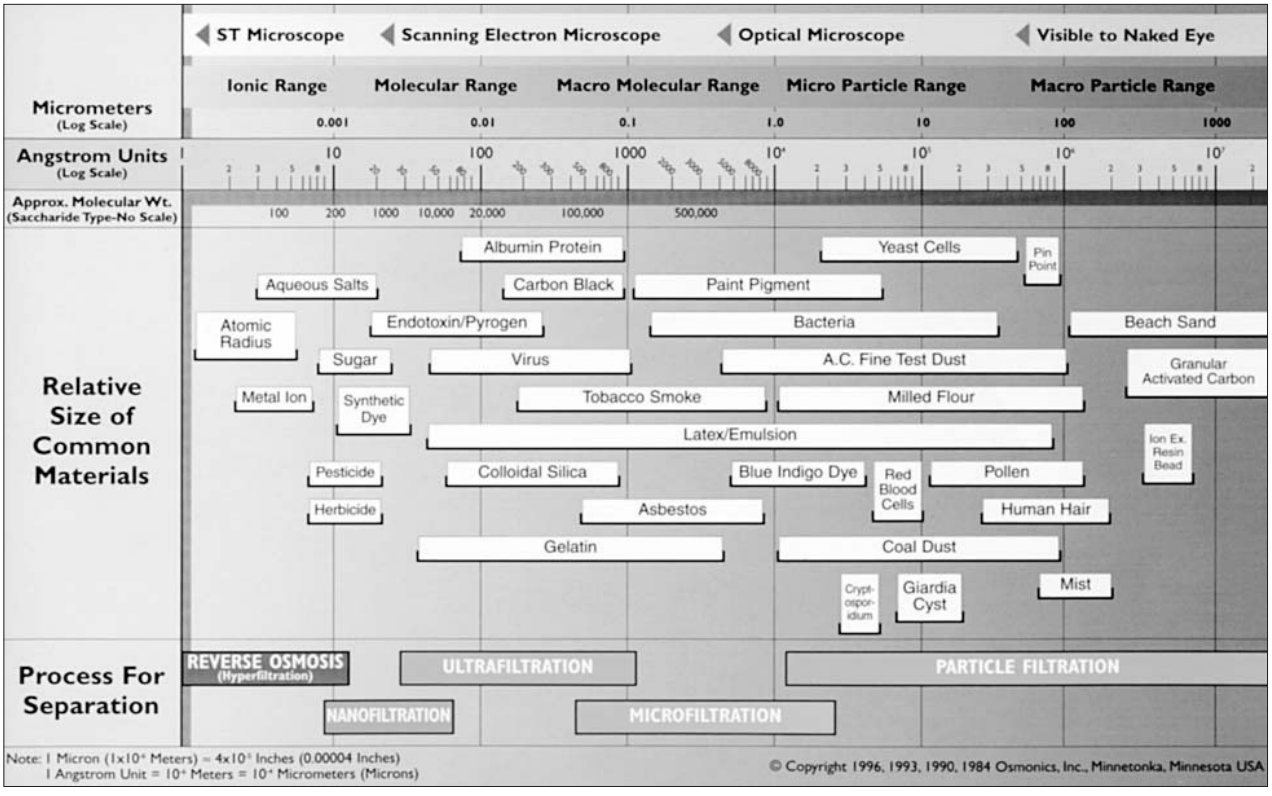


FIG. 22-46 The filtration spectrum. (*Copyright © 1996. Reprinted by permission of Osmonics, Minnetonka, MN.*)

Advantages to Membrane Separation This subsection covers the commercially important membrane applications. All except electrodialysis are pressure driven. All except pervaporation involve no phase change. All tend to be inherently low-energy consumers in theory if not in practice. They operate by a different mechanism than do other separation methods, so they have a unique profile of strengths and weaknesses. In some cases they provide unusual sharpness of separation, but in most cases they perform a separation at lower cost, provide more valuable products, and do so with fewer undesirable side effects than older separations methods. The membrane interposes a new phase between feed and product. It controls the transfer of mass between feed and product. It is a kinetic, not an equilibrium process. In a separation, a membrane will be selective because it passes some components much more rapidly than others. Many membranes are very selective. Membrane separations are often simpler than the alternatives.

General Examples No artificial membrane yet compares to the ones surrounding every cell in nature, but many are very sophisticated in what they do. Thousands of tons of drinking water are produced every day in the Middle East, on islands, and in certain coastal areas by passing pressurized seawater across a very thin membrane that permeates water with practically none of the dissolved salts. Huge quantities of nitrogen are purified from air by membranes operating from the output of a simple, single stage air compressor. Tons of water are purified to an exquisite degree for use in making microchips, most of the purification having been accomplished by passing the water through membranes. Municipalities depend on electrodialysis to remove salt from brackish aquifers to provide high-quality potable water.

Basic Equations All of the processes described in this section depend to some extent on the following background theory. Substances move through membranes by several mechanisms. For porous membranes, such as are used in microfiltration, viscous flow dominates the process. For electrodialytic membranes, the mass transfer is caused by an electrical potential resulting in ionic conduction. For all membranes, Fickian diffusion is of some importance, and it is of dominant importance in gas permeation and reverse osmosis. In the following, almost every step is accompanied by a new assumption. Generally, they are reasonable assumptions, but when using the result, it is important to remember the many assumptions used to reach the convenient form of the equation. The driving force for Fickian transport of a substance is a gradient in chemical potential:

$$N_i = -D_i C \frac{d(\mu_i/RT)}{dx} \tag{22-58}$$

where N_i is the mass of component i transported, kmol/m^2·s, D_i is diffusivity of component i, m^2/s, C is concentration, kmol/m^3, μ_i is chemical potential of the substance diffusing, J/kmol·K, and x is distance, m.

In most cases, activity coefficients are close to one, and Fick's first law is written as:

$$N_i = -D_i \frac{dC_i}{dx} \tag{22-59}$$

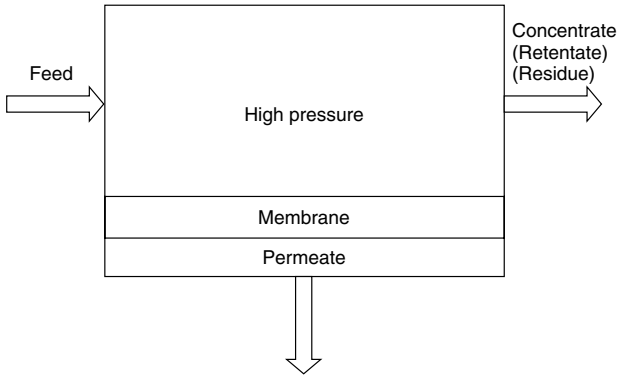
Assuming D_i is constant, and in particular that it is independent of C_i, and that the concentrations in the fluid phases are in equilibrium with the membrane. Fick's law may be written:

$$N_i = D_i \frac{(C_f - C_p)}{z} = D_i \frac{\Delta C}{z} \tag{22-60}$$

where z is the thickness of the membrane active layer, and C_f and C_p are concentrations in the feed and the permeate, respectively. D_i is the diffusivity in the membrane. The concentration of a component in the membrane phase will be quite different than its concentration in the fluid phase even though they are in equilibrium. The diffusivity in the membrane phase will always be much different than it is in the fluid phases, which must be remembered when applying Eq. (22-60). More complete nomenclature is shown in Fig. 22-47.

If Henry's law applies, the concentrations in fluid phases and the membrane are related by:

$$C_i = S \cdot p_i \tag{22-61}$$



Quantity	Feed or high-pressure side	Permeate or low-pressure side	Concentrate, etc.
Flow	$Q_f N$	(J)(A),N	Q_r
Concentration	C_f	C_p	C_c
Partial pressure	p_{feed}	$p_{permeate}$	$p_{residue}$
Gas feed	L	V	R

FIG. 22-47 Schematic of pressure-driven processes showing nomenclature.

where S is a proportionality factor, kmol/m^3·Pa, specific for a membrane and a penetrant and p_i is the partial pressure of component i, Pa.

If the membrane and its immediate surroundings are isothermal (generally except for pervaporation) and if S is a function only of temperature, then:

$$N_i = \left(\frac{S \cdot \overline{D}_i}{z}\right)(p_f - p_p) \tag{22-62}$$

In membrane separations, the product $S \cdot \overline{D}_i$ is referred to as the permeability, ρ_i (kmol/m·s·Pa). The rate of passage of material through a membrane is referred to as flux, with symbol J_i. J_i is equal to N_i in the equations given above. Generally J_i has the dimensions of velocity, m/s (more conveniently, μm/s), or conventionally as ℓ/m^2·hr, gal/ft^2·day, or ft^3/ft^2·day. For most applications, throughput is expressed in volumes instead of moles or mass.

An important consideration is that the "goodness" of the separation is almost independent of the membrane thickness, z, and the *rate* of the process is *inversely* proportional to z, giving rise to a major emphasis on making the separating layer of a membrane very thin. It is rare that z is known for a commercial membrane, and J_i is stated without regard to z.

Basic Concepts

Membrane Porosity Separation membranes run a gamut of porosity (see Fig. 22-48). Polymeric and metallic gas separation membranes, electrodialysis membranes, pervaporation membranes, and reverse osmosis membranes are nonporous, although there is lingering controversy over the nonporosity of the latter. Porous membranes are used for microfiltration and ultrafiltration. Nanofiltration membranes are probably charged porous structures.

Solution-Diffusion Mass passes through nonporous membranes either by ionic conduction (electrodialysis) or by dissolving in the membrane [Eq. (22-61)] then diffusing through the membrane in response to a chemical potential gradient, which may be a change in concentration vapor pressure or an electric potential. Materials have differing Henry's law constants, which was an early emphasis in membrane material selection. Currently, especially in gas membranes, the structural differences leading to enhanced diffusivity selection is an important research area.

Pores Even porous membranes can give very high selectivity. Molecular sieve membranes exist that give excellent separation factors for gases. Their commercial scale preparation is a formidable obstacle. At the other extreme, UF_6 separations use Knudsen flow barriers, with a very low separation factor. Microfiltration (MF) and ultrafiltration (UF) membranes are clearly porous, their pores ranging in size from 3 nm to 3 μm. Nanofiltration (NF) membranes have smaller pores.

TABLE 22-15 Liquid Flux Conversion Factors

To convert	Into	Multiply by	Inverse
U.S. gallons/ft^2·day (gfd)	Liters/m^2·hr (ℓmh)	1.6976	0.5891
gfd	μm/s	0.4715	2.121
ℓmh	μm/s	0.2778	3.600

Separation Factor The separation factor, α, is defined consistent with other separation methods. It is important to recall that in membranes, α is the result of differing rates, and that it has no equilibrium implications. The convention in membrane separations is to define the separation so that $\alpha > 1$.

$$\alpha = \frac{(C_i/C_j)_p}{(C_i/C_j)_f} \tag{22-63}$$

α is widely used in gas separations, and is used occasionally in other separations.

Retention, Rejection, and Reflection **Retention** and **rejection** are used almost interchangeably. A third term, **reflection,** includes a measure of solute-solvent coupling, and is the term used in irreversible thermodynamic descriptions of membrane separations. It is important in only a few practical cases. Rejection is the term of trade in reverse osmosis (RO) and NF, and retention is usually used in UF and MF.

$$R = 1 - \left(\frac{C_p}{C_f}\right) \tag{22-64}$$

where C is the concentration of the material being retained/rejected.

By convention, C_f is measured in the bulk feed, not at the membrane. Clearly, the concentration at the membrane is the important one, but the convention is well established and it simplifies calculations on yield and material balance. Concentration at the membrane, C_{wall} may be calculated by the method shown in Eq. (22-91).

Cross Flow Most membrane processes are operated in cross flow, and only a few have the option to operate in the more conventional dead-end flow. In cross flow, the retentate passes parallel to the separating membrane, often at a velocity an order of magnitude higher than the velocity of the stream passing through the membrane. Microfiltration is the major membrane process in which a significant number if applications may be run with dead-end flow.

Staging Membranes are rarely staged. Except for gas separations, it is unusual for the product to pass through more than one membrane. If the membrane does not make the required separation in one pass, other means of separation will normally be employed. Exceptions are noted for specific applications.

Flux is the term used to describe how fast a product passes through a membrane. A velocity, almost always reported as volume/area-time, it does not take membrane thickness into account. For most users,

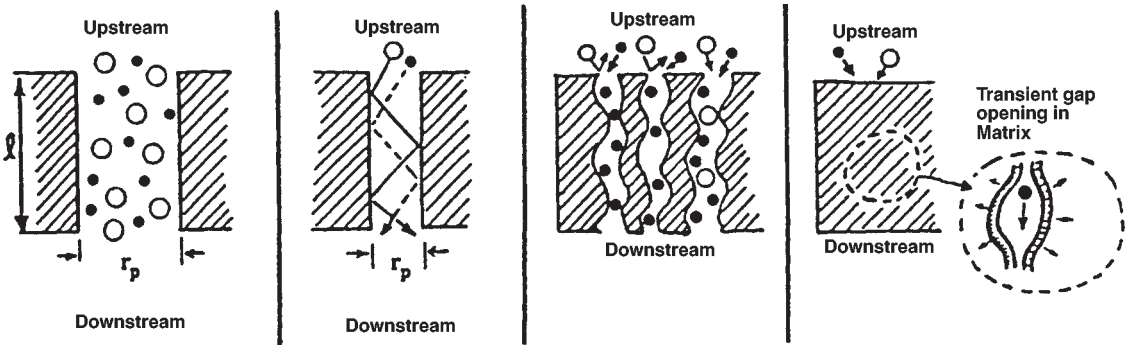


FIG. 22-48 Transport mechanisms for separation membranes: (*a*) Viscous flow, used in UF and MF. No separation achieved in RO, NF, ED, GAS, or PV. (*b*) Knudsen flow used in some gas membranes. Pore diameter < mean free path. (*c*) Ultramicroporous membrane—precise pore diameter used in gas separation. (*d*) Solution-diffusion used in gas, RO, PV. Molecule dissolves in the membrane and diffuses through. Not shown: Electrodialysis membranes and metallic membranes for hydrogen.

membrane thickness is unknown. Flux is specific for the membrane, for the application, for the operating conditions, and usually for time. Some generalization is possible. The rate-limiting step is very different among the operations, and membrane operations have quite different equations for flux.

Fouling Flux declines with time in most membrane operations. A decline to 80 percent of initial output can take minutes or months. The principal cause is fouling, defined as an irreversible decline in output resulting from interaction with components in the feed. "Irreversible" is not synonymous with permanent, and describes a decline that can't be recovered by merely restoring a previous set of process conditions. Cleaning is a common way of restoring much or all of a fouled membrane's former output. Some forms of fouling are permanent, such as those that change membrane structure. Compaction, resulting from polymer creep, is permanent but is not fouling.

Membrane Types A detailed taxonomy of membranes is beyond the scope of this handbook. Membranes may be made from physical solids (metal, ceramic, etc.), homogeneous films (polymer, metal, etc.), heterogeneous solids (polymer mixes, mixed glasses, etc.), solutions (usually polymer), asymmetric structures, and liquids.

Ceramic membranes are quite important since microporous ceramics are the principal barrier in UF_6 separation. Similar devices are used for microfiltration membranes and to a lesser extent for ultrafiltration. Homogeneous films are transformed into microporous devices by irradiation followed by selective leaching of the radiation damaged tracks, by stretching (Gortex® is one well-known example), or by electrochemical attack on aluminum. A few membranes are made by selective leaching of one component from a solid, as in membranes derived from glass or by selective extraction of polymer blends.

Liquid membranes are a specialty, either adsorbed in capillaries or emulsified. They are much studied, but little commercial application is found.

Polymeric membranes dominate the membrane separation field because they are well developed and quite competitive in separation performance and economics. Their usual final form is as **hollow fibers** or **capillaries** or as **flat sheet,** either of which is incorporated into a large module. Fiber-type membranes are solution or melt spun, and undergo some sort of transformation into a membrane shortly after the spinning head. **Thermal inversion** involves quenching a solution to a temperature regime where the polymer precipitates. **Solvent spinning** involves quenching in a nonsolvent, such as water, to produce a highly heterogeneous structure. Flat sheet membrane is made by preparing a casting dope of polymer in solvent, then casting it into a uniform film, then removing the solvent or introducing a nonsolvent (usually both) in such a way as to produce a membrane with a thin, active, separating layer backed by a porous, but mechanically robust sublayer.

An important variant is the composite membrane in which a relatively porous membrane (which often has its own skin) is coated by an even more selective layer, applied by a technique resulting in a very thin separating layer.

Module Types The term "module" is universally used, but the definitions vary. Here, a **module** is the simplest membrane element that can be used in practice. (Figs. 22-48 to 22-53). Module design must deal with five major issues, plus a host of minor ones. First is economy of manufacture. Second, a module must provide support and seals to maintain membrane integrity against damage and leaks. Third, it must deploy the feed stream so as to make intimate contact with the membrane, provide sufficient mass transfer to keep polarization in control, and do so with a minimum waste of energy. Fourth, the module must permit easy egress of permeate. Fifth, the module must permit the membrane to be cleaned when necessary. Many module types have been invented, quite a few were used commercially, but the winning designs as of 1996 are variations on a few simple themes.

Hollow Fiber-Capillary Hollow fiber refers to very small diameter membranes. The most successful one has an outer diameter of only 93 μm and is used for reverse osmosis. Capillary membranes are larger-diameter membranes used for liquid separations. The distinction between them has blurred to the point where there is a virtual continuum of membrane diameters for gases and liquids from the smallest all the way up to 25-mm tubes.

Gas separation membranes have diameters as small as 135 μm outer diameter by 95 μm inner diameter. For low-pressure applications such as air, they may run with tube-side feed. Gas membranes operating at high pressure (above 1.5 MPa) are almost always run with shell-side feed. The outer diameter for gas membranes may be as high as 500 μm.

Self-supported cylindrical membranes for liquid separations are made from 250 μm up to 6 mm, but there is no obvious limit to future offerings. Membrane devices for liquids are almost always tube-side feed, with two major exceptions at the extremes of porosity. High-pressure RO is almost always shell-side feed, and one supplier of very low-pressure MF also runs with shell-side feed.

All types of membrane in this configuration are fashioned into modules by potting the ends with a curable liquid (Figs. 22-49 and 22-50).

Tubular Tubular membranes (Fig. 22-51) are supported by a pressure vessel, usually perforated or porous. It can be as simple as a wrapped nonwoven fabric, or as robust as a stainless-steel tube. All run with tube-side feed. They are mainly used for UF, with some RO applications, particularly for food and dairy. The primary diameters available are 12 and 25 mm. Tubes are often connected in series; parallel bundles, gasketed or potted, are also common.

Monolith Ceramic membranes are usually monoliths of tubular capillaries (Fig. 22-52), although one supplier has square passages. Channel sizes are in the millimeter range. By strict definition, a monolith becomes a module by attaching end fittings and a means of permeate collection. In practice, many monoliths are usually incorporated into one modular housing.

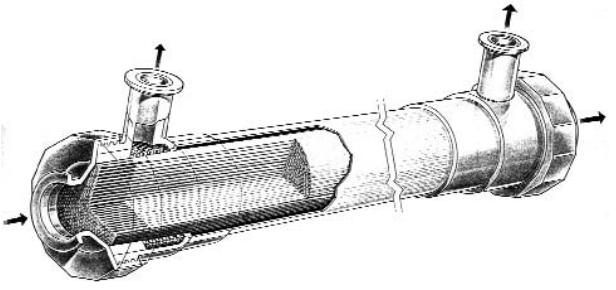


FIG. 22-49 Cutaway view of low-pressure capillary-membrane module. (*Courtesy Pall Corporation.*)

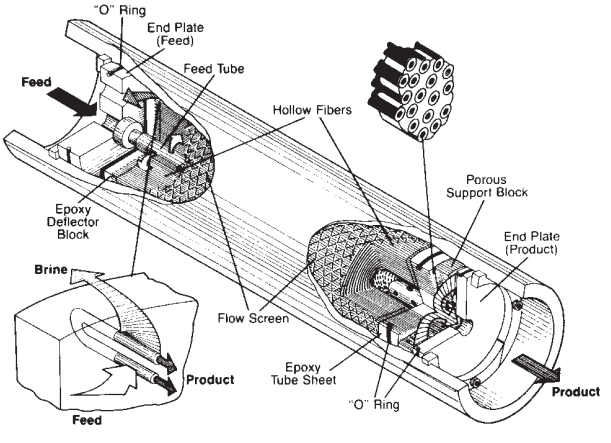


FIG. 22-50 Cutaway view of high-pressure hollow-fine-fiber reverse-osmosis module. (*Courtesy DuPont.*)

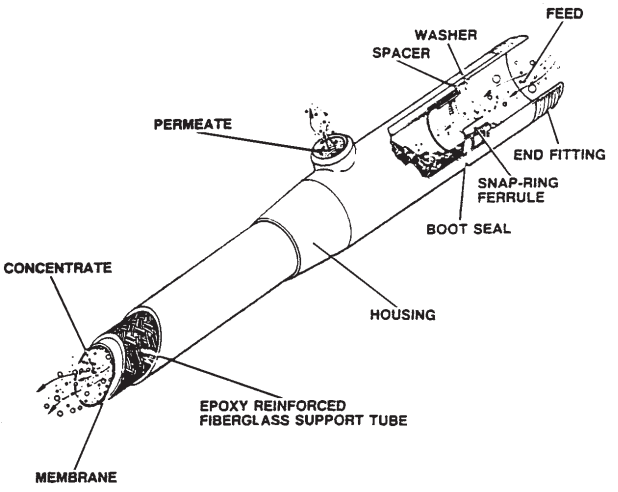


FIG. 22-51 25-mm diameter tubular-membrane assembly. (*Courtesy Koch Membrane Systems.*)

Spiral Flat-sheet membrane may be fashioned into an inexpensive and compact module by spiral winding (Fig. 22-53). Membrane is laminated with a feed spacer separating two sheets of membrane. The permeate side of the membrane contacts a fluid-conductive fabric, in turn connected to a perforated central pipe. The edges are glued to make a complete seal between the feed and permeate sides of the device, and the finished round module is fitted into a pressure vessel where feed enters through one face of the cylinder and leaves through the other. Permeate is collected from the central tube. Multiple leaves are used because the pressure drop in the permeate-conducting fabric becomes limiting at leaf lengths much over 1 m. The spiral-wound membrane module is now a highly evolved device, made as large as 16 inches (400 mm) in diameter, using many leaves. It has slowly increased its market share and is now the dominant design (meaning the "base case" against which other module types are measured) in RO and UF. Spiral-wound modules are occasionally used in gas separation and pervaporation.

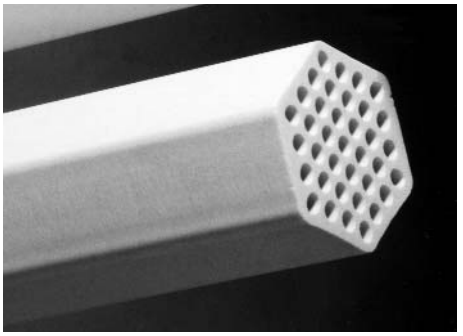


FIG. 22-52 Ceramic element cutaway. Membrane is inside 3 mm circular channels. (*Courtesy SCT/U.S. Filter.*)

Plate-and-Frame Conceptually the simplest, it is very much like a filter press. Once found in RO, UF, and MF, it is still the only module commonly used in electrodialysis (ED). A few applications in pressure-driven membrane separation remain (see Sec. 18 for a description of a plate-and-frame filter press).

Other The cassette (Fig. 22-54), a modification of a plate-and-frame device that is favored because of the ease of scale-up from laboratory to small plants is widely used in pharmaceutical microfiltration and ultrafiltration. An entirely different module also called a **cassette** is used in the MF of water. There are a host of other clever module designs in use, and new ones appear frequently.

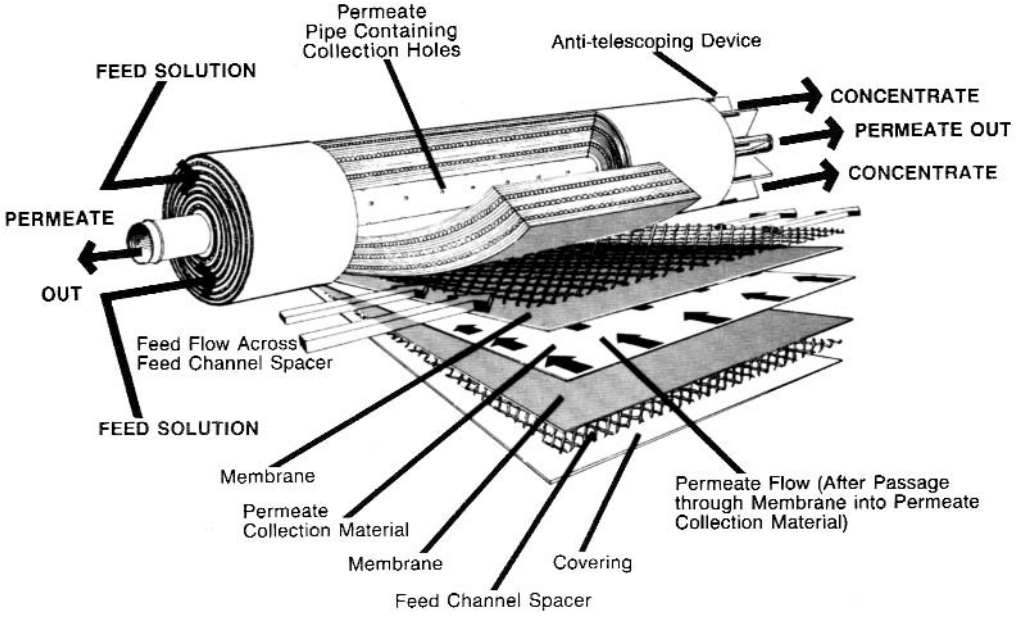


FIG. 22-53 Spiral-wound module used in many membrane processes. Permeate collection material is wound on a perforated permeate pipe. A membrane "sandwich" is constructed over the permeate carrier using glue seams as seals. Membrane "sandwiches" are separated by feed-channel spacers, through which the feed stream is passed. (*Courtesy Koch Membrane Systems.*)

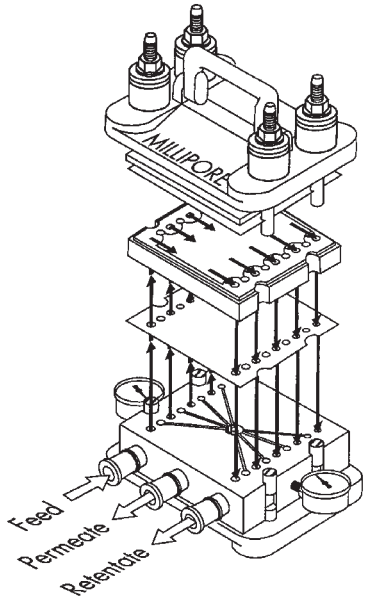


FIG. 22-54 Exploded view of cassette membrane assembly. (*Courtesy Millipore Corporation.*)

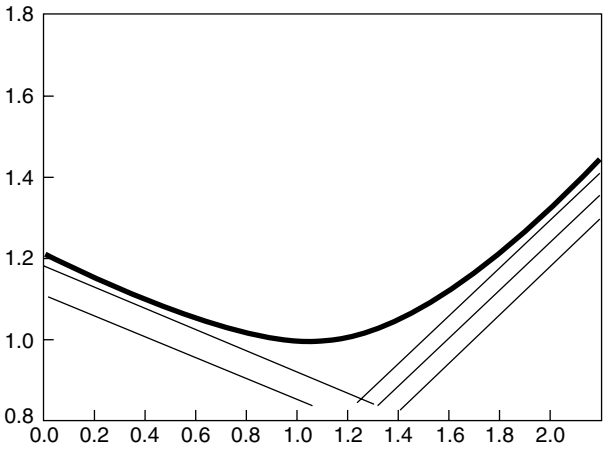


FIG. 22-55 Typical capital-cost schematic for membrane equipment showing trade-off for membrane area and mechanical equipment. Lines shown are from families for parallel lines showing limiting costs for membrane and for ancillary equipment. Abscissa: Relative membrane area installed in a typical membrane process. Minimum capital cost is at 1.0. Ordinate: Relative cost. Line with positive slope is total membrane cost. Line with negative slope is total ancillary equipment cost. Curve is total capital cost. Minimum cost is at 1.0.

Economics The economics of each membrane process are distinct, but there is an underlying concept that is almost universal. What all membrane processes have in common is a membrane device per se, having a characteristic economy of scale cost = r(area)^a, and equipment surrounding and supporting the membrane having an economy of scale cost = s(size)^b. r and s are empirical constants. For all membrane equipment, $a > b$. For almost any membrane separation, there is a trade-off between the amount of membrane area required and the supporting equipment. Where polarization is the rate-limiting step, the designer can put in more pumps, supplying more depolarizing energy, thereby achieving higher fluxes and using less membrane. The result is lower investment for membranes, higher investment for pumps and pipes, higher energy operating costs, and lower membrane replacement costs. Similar arguments apply to operations that are not polarization limited, since they are then limited by some other physical factor such as pressure. In every installation, there is a trade-off between adding more membrane area and more ancillary equipment to make the membrane installed more productive. The values r and s vary with the *kind* of membranes and ancillary equipment used. Systems based on different *kinds* of membranes, ceramic versus organic, for example, will have different multipliers r although the exponent a should be about the same.

Figure 22-55 is a characteristic schematic of the balance between membrane area and ancillary equipment for a particular plant. For actual cases studied, the cost of membrane and its immediately related costs (manifolds, housings, etc.) varied with the 0.9 power of area. The cost of ancillary equipment (pumps, pipes, etc.) varied with the 0.4 power of size. Total capital cost represents the sum of the membrane related and the ancillary equipment, shown in Fig. 22-55 as a curve with a minimum at the point 1, 1. As the curve moves away from the minimum, costs rise approaching a line with slope 0.9 as membrane area increases, representing in the limit the cost of membrane. Moving to the left, the costs approach a line with slope –0.4, representing in the limit the costs of ancillary equipment. It is obvious that every plant needs some of both. For both membrane and ancillary equipment, there will be a series of parallel lines depending on the values of r and s for the different *kinds* of equipment chosen for the separation. For example, substituting a ceramic membrane for an organic membrane does not imply that the *kind* of pumping equipment employed will change. Assuming the ceramic membrane is costlier, using a membrane cost cure shifted upward will change the optimum-cost point, shifting it to the left.

An important caveat: The lines are shown as continuous functions, a considerable oversimplification. Pumps, pipes, valves, and even membrane assemblies come in discrete sizes and capacities, sometimes giving a project cost with a sharper minimum and one displaced from the ideal minimum. Every process has different characteristics, but the general shape of a broad economic minimum is characteristic.

Another similar curve can be drawn for total operating costs. The three biggest elements in operating costs are usually capital charges, membrane replacement, and energy. For most industrial installations, capital charges dominate everything. For municipal and a few other installations, power cost and membrane replacement are often of greater magnitude. Depending on the local economics and the process, the total operating cost minimum may be shifted a bit to the right or the left of the capital cost minimum, but usually not by a great amount. If membrane life is short, the optimum will move left, while if energy is costly, it will move right.

ELECTRODIALYSIS

General References: This section is based on three publications by Heiner Strathmann, to which the interested reader is referred for greater detail [chap. 6, pp. 213–281, in Noble and Stern (eds.), op. cit.; sec. V, pp. 217–262, in Ho and Sirkar, op. cit.; chap. 8, pp. 8-1–8-53, Baker et al., op. cit.].

Process Description *Electrodialysis* (ED) is a membrane separation process in which ionic species are separated from water, macrosolutes, and all uncharged solutes. Ions are induced to move by an electrical potential, and separation is facilitated by ion-exchange membranes. Membranes are highly selective, passing either anions or cations and very little else. The principle of ED is shown in Fig. 22-56.

The feed solution containing ions enters a compartment whose walls are a cation-exchange and an anion-exchange membrane. If the anion-exchange membrane is in the direction of the anode, as shown for the middle feed compartment, anions may pass through that membrane in response to an electrical potential. The cations can likewise

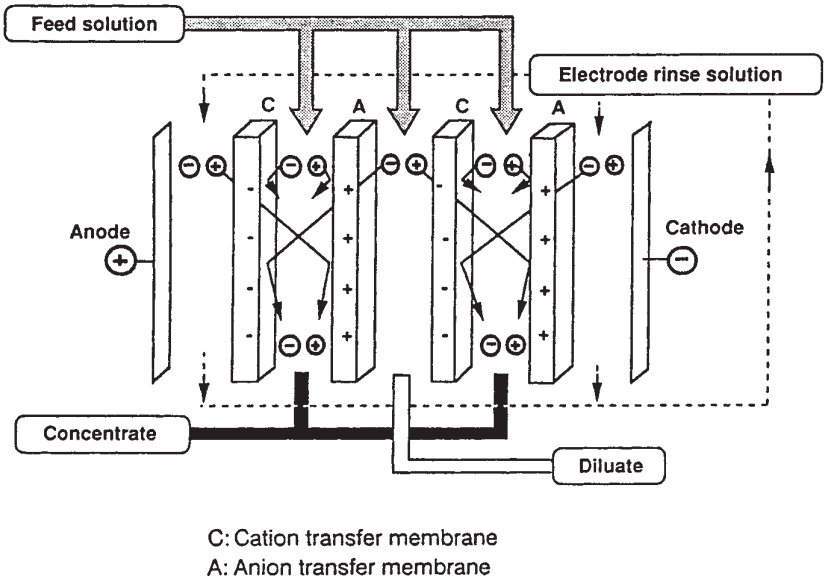


FIG. 22-56 Schematic diagram of electrodialysis. Solution containing electrolyte is alternately depleted or concentrated in response to the electrical field. Feed rates to the concentrate and diluate cells need not be equal. In practice, there would be many cells between electrodes.

move toward the cathode. When the ions arrive in the adjacent compartments, however, their further progress toward the electrodes is prevented by a membrane having the same electrical charge as the ion. The two feed compartments to the left and right of the central compartment are concentrate compartments. Ions entering these two compartments, either in the feed or by passing through a membrane, are retained, either by a same-charged membrane, or by the EMF driving the operation. The figure shows two cells (four membranes) between anode and cathode. In an industrial application, a membrane stack can be composed of hundreds of cells, where mobile ions are alternately being depleted and concentrated.

Many related processes use charged membranes and/or EMF. Electrodialytic water dissociation (water splitting), diffusion dialysis, Donnan dialysis, and electrolysis are related processes. **Electrolysis** (chlorine-caustic) is a process of enormous importance much of which is processed through very special membranes.

Leading Examples Electrodialysis has its greatest use in removing salts from brackish water, where feed salinity is around 0.05–0.5 percent. For producing high-purity water, ED can economically reduce solute levels to extremely low levels as a hybrid process in combination with an ion-exchange bed. ED is not economical for the production of potable water from seawater. Paradoxically, it is also used for the concentration of seawater from 3.5 to 20 percent salt. The concentration of monovalent ions and selective removal of divalent ions from seawater uses special membranes. This process is unique to Japan, where by law it is used to produce essentially all of its domestic table salt. ED is very widely used for deashing whey, where the desalted product is a useful food additive, especially for baby food.

Many ED-related processes are practiced on a small scale, or in unique applications. Electrodialysis may be said to do these things well: separate electrolytes from nonelectrolytes and concentrate electrolytes to high levels. It can do this even when the pH is very low. ED does not do well at: removing the last traces of salt (although the hybrid process, electrodeionization, is an exception), running at high pH, tolerating surfactants, or running under conditions where solubility limits may be exceeded. Hydroxyl ion and especially hydrogen ion easily permeate both types of ED membrane. Thus, processes that generate a pH gradient across a membrane are limited in their scope.

Water splitting, a closely related process, is useful for reconstituting an acid and a base out of a salt. It is used to reclaim salts produced during neutralization.

Membranes Ion-exchange membranes are highly swollen gels containing polymers with a fixed ionic charge. In the interstices of the polymer are mobile counterions. A schematic diagram of a cation-exchange membrane is depicted in Fig. 22-57.

Figure 22-57 is a schematic diagram of a cation-exchange membrane. The parallel, curved lines represent the polymer matrix composed of an ionic, crosslinked polymer. Shown in the polymer matrix are the fixed negative charges on the polymer, usually from sulfonate groups. The spaces between the polymer matrix are the water-swollen interstices. Positive ions are mobile in this phase, but negative ions are repelled by the negative charge from the fixed charges on the polymer.

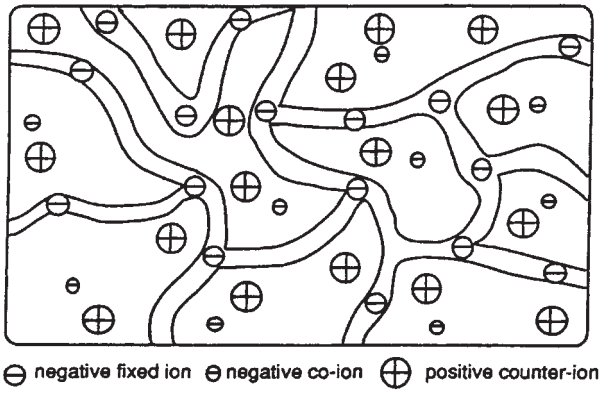


FIG. 22-57 Schematic diagram of a cation-exchange membrane showing the polymer matrix with fixed negative charges and mobile positive counterions. The density of fixed negative charges is sufficient to prevent the passage (exchange) of anions.

In addition to high permselectivity, the membrane must have low-electrical resistance. That means it is conductive to counterions and does not unduly restrict their passage. Physical and chemical stability are also required. Membranes must be mechanically strong and robust, they must not swell or shrink appreciably as ionic strength changes, and they must not wrinkle or deform under thermal stress. In the course of normal use, membranes may be expected to encounter the gamut of pH, so they should be stable from $0 < pH < 14$ and in the presence of oxidants.

Optimization of an ion-exchange membrane involves major trade-offs. Mechanical properties improve with cross-link density, but so does high electrical resistance. High concentration of fixed charges favors low electrical resistance and high selectivity, but it leads to high swelling, thus poor mechanical stability. Membrane developers try to combine stable polymeric backbones with stable ionic functional groups. The polymers are usually hydrophobic and insoluble. Polystyrene is the major polymer used, with polyethylene and polysulfone finding limited application.

Most commercial ion-exchange membranes are homogeneous, produced either by polymerization of functional monomers and cross-linking agents, or by chemical modification of polymers. Many heterogeneous membranes have been prepared both by melting and pressing a mixture of ion-exchange resin and nonfunctional polymer, or by dissolving or dispersing both functional and support resins in a solvent and casting into a membrane. Microheterogeneous membranes have been made by block and graft polymerization.

No membrane and no set of membrane properties has universal applicability. Manufacturers who service multiple applications have a variety of commercial membranes. One firm lists twenty different membranes having a broad spectrum of properties.

Cation-Exchange Membranes Polystyrene copolymerized with divinylbenzene, then sulfonated, is the major building block for cation-exchange membranes. These membranes have reasonable stability and versatility and are highly ionized over most of the pH range. Other chemistries mentioned in the literature include carboxylic acid membranes based on acrylic acid, PO_3^{2-}, HPO_2^-, AsO_3^{2-}, and SeO_3^-. Many specialty membranes have been produced for electrodialysis applications. A notable example is a membrane selective to monovalent cations made by placing a thin coating of positive charge on the cation-exchange membrane. Charge repulsion for polyvalent ions is much higher than that for monovalent ions, but the resistance of the membrane is also higher.

Anion-Exchange Membranes Quaternary amines are the major charged groups in anion-exchange membranes. Polystyrene-divinylbenzene polymers are common carriers for the quaternary amines. The literature mentions other positive groups based on N, P, and S. Anion-exchange membranes are problematic, for the best cations are less robust chemically than their cation exchange counterparts. Since most natural foulants are colloidal polyanions, they adhere preferentially to the anion-exchange membrane, and since the anion-exchange membrane is exposed to higher local pH there is a greater likelihood that precipitates will form there.

Membrane Efficiency The permselectivity of an ion-exchange membrane is the ratio of the transport of electric charge through the membrane by specific ions to the total transport of electrons. Membranes are not strictly semipermeable, for coions are not completely excluded, particularly at higher feed concentrations. For example, the Donnan equilibrium for a univalent salt in dilute solution is:

$$C_{Co}^{M} = \left(\frac{(C_{Co}^{F})^2}{C_R^M} \right) \left(\frac{\gamma_{\pm}^{F}}{\gamma_{\pm}^{M}} \right)^2 \tag{22-65}$$

where C_{Co}^{M} is the concentration of coions (the ions having the same electrical charge as the fixed charges on the membrane); C_{Co}^{F} is the concentration of such coions in the ambient solution; C_R^M is the concentration of fixed charges in the gel water of the membrane; and $\gamma_{\pm}^{F}$ and $\gamma_{\pm}^{M}$ are respectively the geometric mean of the activity coefficients of the salt ions in the ambient solution and in the membrane. Equation (22-65) is applicable only when $C_{Co}^{F} \ll C_R^M$. Since the membrane properties are constant, coion transport rises roughly with the square of concentration.

Process Description Figure 22-58 gives a schematic view of an ED cell pair, showing the salt-concentration profile. In the solution compartment on the left, labeled "Diluate," anions are being attracted to the right by the anode. The high density of fixed cations in membrane "A" is balanced by a high mobile anion concentration within it. Cations move toward the cathode at the left, and there is a similar high mobile cation concentration in the fixed anion membrane "C" separating the depleting compartment from the concentrating compartment further left (not shown). For the anion permeable membrane "A," two boundary layers are shown. They represent depletion in the boundary layer on the left, and an excess in the boundary layer on the right, both due to the concentration polarization effects common to all membrane processes—ions must diffuse through a boundary layer whether they are entering or leaving a membrane. That step must proceed down a concentration gradient.

With every change in ion concentration, there is an electrical effect generated by an electrochemical cell. The anion membrane shown in the middle has three cells associated with it, two caused by the concentration differences in the boundary layers, and one resulting from the concentration difference across the membrane. In addition, there are ohmic resistances for each step, resulting from the E/I resistance through the solution, boundary layers, and the membrane. In solution, current is carried by ions, and their movement produces a friction effect manifested as a resistance. In practical applications, I^2R losses are more important than the power required to move ions to a compartment with a higher concentration.

Transfer of Ions Mass transfer of ions in ED is described by many electrochemical equations. The equations used in practice are empirical. If temperature, the flux of individual components, elec-

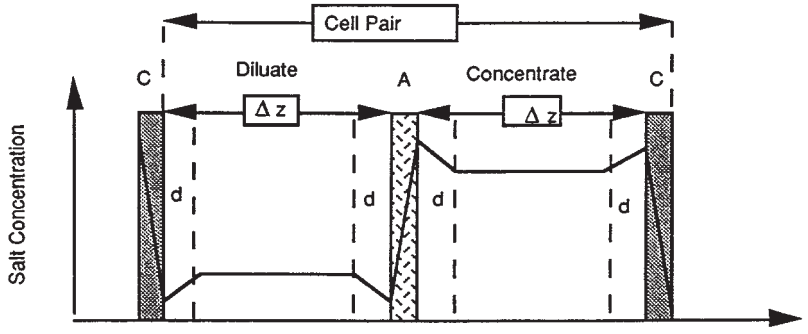


FIG. 22-58 Concentration profile of electrolyte across an operating ED cell. Ion passage through the membrane is much faster than in solution, so ions are enriched or depleted at the cell-solution interface. "d" is the concentration boundary layer. The cell gap, Δz should be small. The ion concentration in the membrane proper will be much higher than shown. (*Courtesy Elsevier.*)

troosmotic effects, streaming potential and other indirect effects are minor, an equation good to a reasonable level of approximation is:

$$J_n = C_{mn} U_{mn} \Delta\varphi/\Delta x \qquad (22\text{-}66)$$

where J is the component flux through the membrane kmol/m^2·s, C_{mn} is the concentration in phase m of component n, kmol/m^3, U_{mn} is the ion mobility of n in m, m^2/v·s, φ is the electrical potential, volts, and x is distance, m.

Equation (22-66) assumes that all mass transport is caused by an electrical potential difference acting only on cations and anions. Assuming the transfer of electrical charges is due to the transfer of ions.

$$i = F \sum_n |z_n J_n| \qquad (22\text{-}67)$$

where i is the current density, amperes/m^2, F is the Faraday constant and z is the valence. The transport number, T, is the ratio of the current carried by an ion to the current carried by all ions.

$$T_n = \frac{J_n z_n}{\sum_n J_n z_n} \qquad (22\text{-}68)$$

The transport number is a measure of the permselectivity of a membrane. If, for example, a membrane is devoid of coions, then all current through the membrane is carried by the counterion, and the transport number = 1. The transport numbers for the membrane and the solution are different in practical ED applications.

Concentration Polarization As is shown in the flow schematic, ions are depleted on one side of the membrane and enriched on the other. The ions leaving a membrane diffuse through a boundary layer into the concentrate, so the concentration of ions will be higher at the membrane surface, while the ions entering a membrane diffuse through a boundary layer from the diluate, so the bulk concentration in the diluate must be higher than it is at the membrane. These effects occur because the transport number of counterions in the membrane is always very much higher than their transport number in the solution. Were the transport numbers the same, the boundary layer effects would vanish. This concentration polarization is similar to that experienced in reverse osmosis, except that it has both depletion and enrichment components. The equations governing concentration polarization and depolarization of a membrane are given in the section describing ultrafiltration. The depolarizing strategies used for ED are similar to those employed in other membrane processes, as they involve induced flow past the membrane.

Two basic flow schemes are used: tortuous path flow and sheet flow (Fig. 22-59). Tortuous path spacers are cut to provide a long path between inlet and outlet, providing a relatively long residence time and high velocity past the membrane. The flow channel is open. Sheet flow units have a net spacer separating the membranes. Mass transfer is enhanced either by the spacer or by higher velocity.

Enhanced depolarization requires capital equipment and energy, but it achieves savings in overall capital costs (permits the use of a smaller stack) and energy (permits lower voltage.) The designer's task is to achieve an optimum balance in these requirements. Sheet-flow units have lower capital and operating costs in general, yet both sheet-flow and tortuous-flow units remain competitive. The fact that most ED reversal units (see below) are tortuous flow, and that ED reversal is the dominant technology for water and many waste treatment applications may explain the paradox.

Limiting Current Density As the concentration in the diluate becomes ever smaller, or as the current driving the process is increased, eventually a situation arises in which the concentration of ions at the membranes surrounding the diluate compartment approaches zero. When that occurs, there are insufficient ions to carry additional current, and the cell has reached the limiting current. Forcing the voltage higher results in the dissociation of water at the membrane, giving rise to a dramatic increase in pH due to OH^- ions emerging from the anion-exchange membrane. The high pH promotes precipitation of metal hydroxides and $CaCO_3$ on the membrane surface leading to flow restrictions, poor mass transfer, and subsequent membrane damage. Once a precipitate forms, its presence initiates a vicious cycle fostering the formation of more precipitates. The general expression for the limiting current density is $i_{\lim} \sim (C_{\text{bulk diluate}})$ (diluate velocity)^m, where m is an experimental constant (often 0.6). Thus, the concentration at the membrane is limiting, and at constant current that is proportional to the bulk concentration and the mass-transfer coefficient. Flow in the compartment is laminar but mass transfer is enhanced by the spacer. A normal operating practice is to operate a stack at around 75 percent of the limiting current.

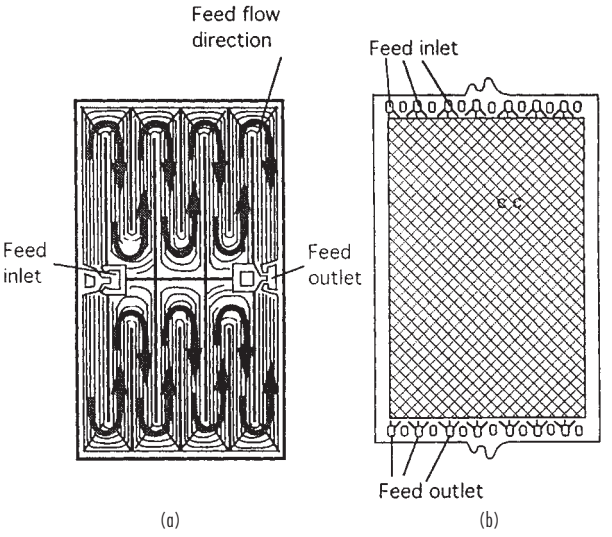


FIG. 22-59 Schematic of two ways to pass solution across an ED membrane. Tortuous flow (left) uses a special spacer to force the solution through a narrow, winding path, raising its velocity, mass transfer, and pressure drop. Sheet feed (right) passes the solution across the plate uniformly, with lower pressure drop and mass transfer. (*Courtesy Elsevier.*)

Process Configuration Figure 22-56 shows a basic cell pair. A stack is an assembly of many cell pairs, electrodes, gaskets, and manifolds needed to supply them. An exploded schematic of a portion of a sheet-flow stack is shown in Fig. 22-60.

Gaskets are very important, since they not only keep the streams separated and prevent leaks from the cell, they have the manifolds to conduct feeds, both concentrate and diluate, built into them. No other practical means of feeding the stack is used in the very cramped space required by the need to keep cells thin because the diluate has very low conductivity. The manifolds are formed by aligning holes in membrane and gasket.

The membranes are supported and kept apart by feed spacers. A typical cell gap is 0.5–2 mm. The spacer also helps control solution distribution and enhances mass transfer to the membrane. Given that an industrial stack may have up to 500 cell pairs, assuring uniform flow distribution is a major design requirement.

Since electrodialysis membranes are subject to fouling, it is sometimes necessary to disassemble a stack for cleaning. Ease of reassembly is a feature of ED.

Process Flow The schematic in Fig. 22-56 may imply that the feed rates to the concentrate and diluate compartments are equal. If they are, and the diluate is essentially desalted, the concentrate would leave the process with twice the salt concentration of the feed. A higher ratio is usually desired, so the flow rates of feed for concentrate and feed for diluate can be independently controlled. Since sharply differing flow rates lead to pressure imbalances within the stack, the usual procedure is to recirculate the brine stream using a feed-and-bleed technique This is usually true for ED reversal plants. Some nonreversal plants use slow flow on the brine side avoiding the recirculating pumps.. Diluate production rates are often 10× brine-production rates.

Electrodes No matter how many cells are put in series, there will be electrodes. The more cells, the less the relative importance of the

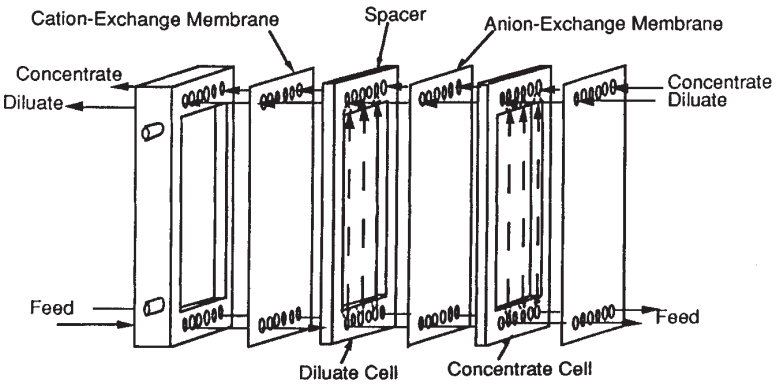


FIG. 22-60 Exploded view of a sheet-feed ED stack. Manifolds are built into the membranes and spacers as the practical way to maintain a narrow cell gap. (*Courtesy Elsevier.*)

electrodes. The cathode reactions are relatively mild, and depending on the pH:

$$2H^+ + 2e^- \rightarrow H_2$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

Anode reactions can be problematic. The anode may dissolve or be oxidized. Or, depending on the pH and the chloride concentration:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Dissolution of metal is avoided by selecting a resistant material such as Pt, Pt coated on Ti, or Pt on Nb. Base metals are sometimes used, as are graphite electrodes.

Electrode isolation is practiced to minimize chlorine production and to reduce fouling. A flush solution free of chlorides or with reduced pH is used to bathe the electrodes in some plants. Further information on electrodes may be found in a work by David ["Electrodialysis," pp. 496–499, in Porter (ed.), op. cit.].

Peripheral Components In addition to the stack, a power supply, pumps for diluate and concentrate, instrumentation, tanks for cleaning, and other peripherals are required. Safety devices are mandatory given the dangers posed by electricity, hydrogen, and chlorine.

Pretreatment Feed water is pretreated to remove gross objects that could plug the stack. Additives that inhibit the formation of scale, frequently acid, may be introduced into the feed.

Electrodialysis Reversal Two basic operating modes for ED are used in large-scale installations. **Unidirectional operation** is the mode described above in the general explanation of the process. The electrodes maintain their polarity and the ions always move in a constant direction. **ED reversal** is an intermittent process in which the polarity in the stack is reversed periodically. The interval may be from several minutes to several hours. When the polarity is reversed, the identity of compartments is also reversed, and diluate compartments become concentrate compartments and vice versa. The scheme requires instruments and valves to redirect flows appropriately after a reversal. The advantages that often justify the cost are a major reduction in membrane scaling and fouling, a reduction in feed additives required to prevent scaling, and less frequent stack-cleaning requirements.

Water Splitting A modified electrodialysis arrangement is used as a means of regenerating an acid and a base from a corresponding salt. For instance, NaCl may be used to produce NaOH and HCl. Water splitting is a viable alternative to disposal where a salt is produced by neutralization of an acid or base. Other potential applications include the recovery of organic acids from their salts and the treating of effluents from stack gas scrubbers. The new component required is a bipolar membrane, a membrane that splits water into H^+ and OH^-. At its simplest, a bipolar membrane may be prepared by laminating a cation and an anion membrane. In the absence of mobile ions, water sorbed in the membrane splits into its components when a sufficient electrical gradient is applied. The intimate contact of the two membranes minimizes the problem of the low ionic conductivity of ion-depleted water. As the water is split, replacement water readily diffuses from the surrounding solution. Properly configured, the process is energy efficient.

A schematic of the production of acid and base by electrodialytic water dissociation is shown in Fig. 22-61. The bipolar membrane is inserted in the ED stack as shown. Salt is fed into the center compartment, and base and acid are produced in the adjacent compartments. The bipolar membrane is placed so that the cations are paired with OH^- ions and the anions are paired with H^+. Neither salt ion penetrates the bipolar membrane. As is true with conventional electrodialysis, many cells may be stacked between the anode and the cathode.

If recovery of both acid and base is unnecessary, one membrane is left out. For example, in the recovery of a weak acid from its salt, the anion-exchange membrane may be omitted. The process limitations relate to the efficiency of the membranes, and to the propensity for H^+ and OH^- to migrate through membranes of like fixed charge, limiting the attainable concentrations of acid and base to 3–5 N. The problem is at its worst for HCl and least troublesome for organic acids. Ion leakage limits the quality of the products, and the regenerated acids and bases are not of high enough quality to use in regenerating a mixed-bed ion-exchange resin.

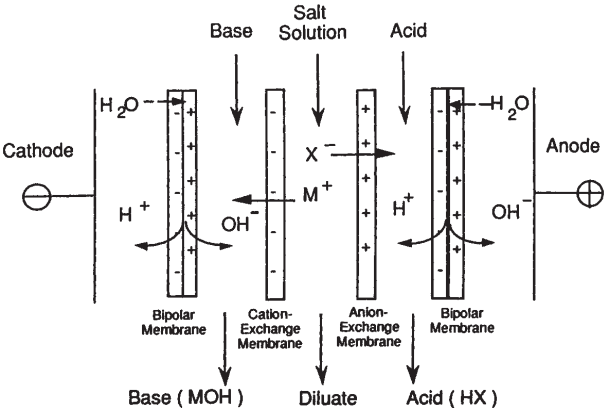


FIG. 22-61 Electrodialysis water dissociation (water splitting) membrane inserted into an ED stack. Starting with a salt, the device generates the corresponding acid and base by supplying H^+ and OH^- from the dissociation of water in a bipolar membrane. (*Courtesy Elsevier.*)

Diffusion Dialysis The propensity of H^+ and OH^- to penetrate membranes is useful in diffusion dialysis. An anion-exchange membrane will block the passage of metal cations while passing hydrogen ions. This process uses special ion-exchange membranes, but does not employ an applied electric current.

As an example, in the aircraft industry heavy-aluminum sections are shaped as airfoils, then masked. The areas where the metal is not required to be strong are then unmasked and exposed to NaOH to etch away unneeded metal for weight reduction. Sodium aluminate is generated, a potential waste problem. Cation-exchange membranes leak OH^- by a poorly understood mechanism that is not simply the transport of OH^- with its waters of hydration. The aluminate anion is retained in the feed stream while the caustic values pass through. NaOH recovery is high, because all the Na^+ participates in the driving force. There is considerable passage of water due to the osmotic pressure difference as well. This scheme operates efficiently only because aluminum hydroxide forms highly supersaturated solutions. Hydroxide precipitation within the apparatus is reported to be a minor problem. $Al(OH)_3$ is precipitated in a downstream crystallizer, and is reported to be of high quality.

Donnan Dialysis Another nonelectrical process using ED membranes is used to exchange ions between two solutions. The common application is to use H^+ to drive a cation from a dilute compartment to a concentrated one. A schematic is shown in Fig. 22-62. In the right compartment, the pH is 0, thus the H^+ concentration is 10^7 higher than in the pH 7 compartment on the left. H^+ diffuses leftward, creating an electrical imbalance that can only be satisfied by a cation diffusing rightward through the cation-selective membrane. By this scheme, Cu^{++} can be "pumped" from left to right against a significant concentration difference.

Electrodialysis-Moderated Ion Exchange The production of ultrapure water is facilitated by incorporating a mixed-bed ion-exchange resin between the membranes of an ion-exchange stack. Already pure water is passed through the bed, while an electric current is passed through the stack. Provided the ion-exchange beads are in contact with each other and with the membranes, an electrical current can pass through the bed even though the conductivity of the very pure water is quite low. In passing, the current conducts any ions present into adjacent compartments, simultaneously and continuously regenerating the resin in situ.

Energy Requirements The thermodynamic limit on energy is the ideal energy needed to move water from a saline solution to a pure phase. The theoretical minimum energy is given by:

$$\Delta G = RT \ln (a/a_s) \tag{22-69}$$

where ΔG is the Gibbs free energy required to move one mole of water from a solution, a is the activity of pure water ($\equiv 1$), and a_s is the activity of water in the salt solution. In a solution, the activity of water is approximately equal to the molar fraction of water in the solution. So that approximate activity is:

$$a_s = \frac{n_s}{n_s + \nu \cdot s_s} \qquad \frac{1}{a_s} = 1 + \frac{\nu \cdot s_s}{n_s} \tag{22-70}$$

where n_s is the number of moles of water in the salt solution, ν is the number of atoms in the salt molecule (2 for NaCl, 3 for $CaCl_2$) and s_s is the number of moles of salt in the salt solution. The ratio of moles of salt in the salt solution to the number of moles of water in the salt solution is a very small number for a dilute solution. This permits using the approximation $\ln(1+x) = x$, when x is of the magnitude 0.01, making this an applicable approximation for saline water. That permits rewriting Eq. (22-69) as:

$$\Delta G = \nu RT(s_s/n_s) \tag{22-71}$$

where ΔG is still the free energy required to move one mole of water from the saline solution to the pure water compartment.

The conditions utilized in the above development of minimum energy are not sufficient to describe electrodialysis. In addition to the desalination of water, salt is moved from a saline feed to a more concentrated compartment. That free-energy change must be added to the free energy given in Eq. (22-71), which describes the movement of water from salt solution, the reverse of the actions in the diluate compartment (but having equal free energy). *Schaffer & Mintz* develop that change, and after solving the appropriate material balances, they arrive at a practical simplified equation for a monovalent ion salt, where activities may be approximated by concentrations:

$$\Delta G = RT(C_f - C_d)\left(\frac{\ln C_{fc}}{C_{fc} - 1} - \frac{\ln C_{fd}}{C_{fd} - 1}\right); \; C_{fc} = \frac{C_f}{C_c}; \; C_{fd} = \frac{C_f}{C_d} \tag{22-72}$$

where C_f is the concentration of ions in the feed, C_d is the concentration in the diluate, and C_c is the concentration in the concentrate, all in kmol/m^3. When $C_{fc} \to 1$ and $C_{fd} \to$ infinity, the operation is one approximating the movement of salt from an initial concentration into an unlimited reservoir of concentrate, while the diluate becomes pure. This implies that the concentrate remains at a constant salt concentration. In that case, Eq. (22-72) reduces to $RT(C_f - C_d)$. As a numerical example of Eq. (22-72) consider the desalting of a feed with initial concentration 0.05 M to 0.005 M, roughly approximating the production of drinking water from a saline feed. If 10 ℓ of product are produced for every 3 ℓ of concentrate, the concentrate leaves the process at 0.2 M. The energy calculated from Eq. (22-72) is 0.067 kWh/m^3 at 25°C. If the concentrate flow is infinite, $C_c = 0.05$ M, and the energy decreases to 0.031 kWh/m^3.

This minimum energy is that required to move ions only, and that energy will be proportional to the ionic concentration in the feed. It assumes that all resistances are zero, and that there is no polarization. In a real stack, there are several other important energy dissipaters. One is overcoming the electrical resistances in the many components. Another is the energy needed to pump solution through the stack to reduce polarization and to remove products. Either pumping or desalting energy may be dominant in a working stack.

Energy Not Transporting Ions Not all current flowing in an electrodialysis stack is the result of the transport of the intended ions. Current paths that may be insignificant, minor, or significant include electrical leakage through the brine manifolds and gaskets, and transport of co-ions through a membrane. A related indirect loss of current is water transport through a membrane either by osmosis or with solvated ions, representing a loss of product, thus requiring increased current.

Pump Energy Requirements If there is no forced convection within the cells, the polarization limits the current density to a very uneconomic level. Conversely, if the circulation rate is too high, the energy inputs to the pumps will dominate the energy consumption of the process. Furthermore, supplying mechanical energy to the cells raises the pressure in the cells, and raises the pressure imbalance between portions of the stack, thus the requirements of the confining gear and the gaskets. Also, cell plumbing is a design problem made more difficult by high circulation rates.

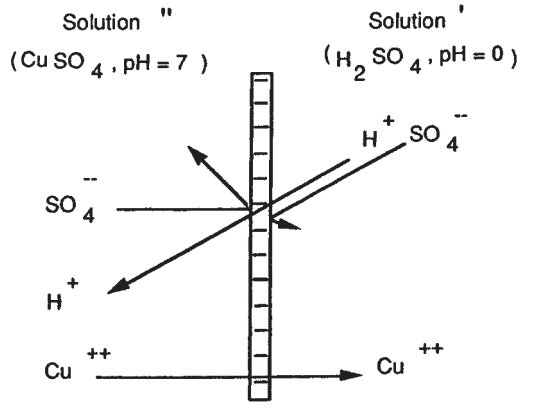


FIG. 22-62 Schematic of Donnan dialysis using a cation-exchange membrane. Cu^{2+} is "pumped" from the lower concentration on the left to a higher concentration on the right maintaining electrical neutrality accompanying the diffusion of H^+ from a low pH on the right to a higher pH on the left. The membrane's fixed negative charges prevent mobile anions from participating in the process. (*Courtesy Elsevier.*)

A rule of thumb for a modern ED stack is that the pumping energy is roughly 0.5 kWh/m^3, about the same as is required to remove 1700 mg/ℓ dissolved salts.

Equipment and Economics A very large electrodialysis plant would produce 500 ℓ/s of desalted water. A rather typical plant was built in 1993 to process 4700 m^3/day (54.4 ℓ/s). Capital costs for this plant, running on low-salinity brackish feed were $1,210,000 for all the process equipment, including pumps, membranes, instrumentation, and so on. Building and site preparation cost an additional $600,000. The building footprint is 300 m^2. For plants above a threshold level of about 40 m^3/day, process-equipment costs usually scale at around the 0.7 power, not too different from other process equipment. On this basis, process equipment (excluding the building) for a 2000 m^3/day plant would have a 1993 predicted cost of $665,000.

The greatest operating-cost component, and the most highly variable, is the charge to amortize the capital. Many industrial firms use capital charges in excess of 30 percent. Some municipalities assign long amortization periods and low-interest rates, reflecting their cost of capital. Including buildings and site preparation, the range of capital charges assignable to 1000 m^3 of product is $90 to $350.

On the basis of 1000 m^3 of product water, the operating cost elements (as shown in Table 22-16) are anticipated to be:

TABLE 22-16 Electrodialysis Operating Costs

$ 66	Membrane-replacement cost (assuming seven-year life)
32	Plant power
16	Filters and pretreatment chemicals
11	Labor
8	Maintenance
$133	Total

These items are highly site specific. Power cost is low because the salinity removed by the selected plant is low. The quality of the feed water, its salinity, turbidity, and concentration of problematic ionic and fouling solutes, is a major variable in pretreatment and in conversion.

REVERSE OSMOSIS AND NANOFILTRATION

Process Description *Reverse osmosis* (RO) and *nanofiltration* (NF) processes utilize a membrane that selectively restricts flow of solutes while permitting flow of the solvent. The processes are closely related, and NF is sometimes called "loose RO." They are kinetic processes, not equilibrium processes. The solvent is almost always water.

Leading Examples

Potable Water RO and NF both play a major role in providing potable water, defined either by the WHO criterion of <1000 ppm *total dissolved solids* (TDS) or the U.S. EPA limit of 500 ppm TDS. RO is most prominent in the Middle East and on islands where potable-water demand has outstripped natural supply. A plant awaiting startup at Al Jubail, Saudi Arabia produces over 1 m^3/s of fresh water (see Table 22-17). Small units are found on ships and boats. Seawater RO competes with *multistage flash distillation* (MSF) and *multieffect distillation* (MED) (see Sec. 13: "Distillation"). It is too expensive to compete with conventional civil supply (canals, pipelines, wells) in most locations. Low-pressure RO and NF compete with electrodialysis for the desalination of brackish water. The processes overlap economically, but they are sufficiently different so that the requirements of the application often favor one over the others.

TABLE 22-17 Water Volume Conversion Factors

To convert	Into	Multiply by	Inverse
1000 U.S. gallons	Cubic meters	3.785	0.2642
Acre-feet	Cubic meters	1233	8.11×10^{-4}
100 cubic feet	Cubic meters	2.831	0.3532
k-gal/day	m^3/s	4.381×10^{-5}	22,827
MGD	m^3/s	4.381×10^{-2}	22.827

Ocean water has an osmotic pressure of about 2.6 MPa, with some locations as high as 3.5 MPa. Recovery (r) is normally around 45 percent, occasionally higher. Osmotic pressure in the concentrate rises as $1/(1 - r)$ and significant overpressure (at least 1 MPa) is required to maintain good-quality permeate. Normal operating pressures are 6–8 MPa.

Brackish water has lower TDS than seawater. It ranges from diluted seawater to natural sources containing various salts. Some of the sources are quite large, and they may provide an attractive supplemental source of potable water. Disposal of the concentrate (brine) can be a problem for inland aquifers.

Where the TDS in water supplies is above the taste threshold, or where there is concern about the safety of the water supply, simple RO systems operating on line pressure have made a major impact. These compact units are usually kitchen installed, and are simple, small, and cheap. For typical line pressure of 400 kPa, 95 percent reduction of TDS is feasible if the inlet concentration is below 2000 mg/ℓ.

Process Water Purification Boiler feed water is a major process application of RO. Scalants and colloids are particularly well rejected by membranes, and TDS is reduced to a level that makes ion exchange or continuous deionization for the residual ions very economical. Even the extremely high quality water required for nuclear power plants can be made from seawater. The ultra-high quality water required for production of electronic microcircuits is usually processed starting with two RO systems operating in series, followed by many other steps.

Process Dewatering Applications RO is useful in many small applications where there is a volume of water containing a small amount of contaminant. RO is often able to recover most of the water at a purity high enough for reuse. The waste is concentrated making its disposal less costly, which generally pays for the recovery process.

Food and Beverage Applications RO achieved modest success in dewatering and concentrating food streams. The first food application pursued by early workers was the dewatering of orange juice prior to freezing. Cheryan [in Noble and Stern (eds.), op. cit., p. 452] describes a proprietary process that achieves high quality and high concentration by removing the flavor-laden phase first, concentrating the sugar stream with tight RO, then at high sugar concentrations using looser membranes to reduce $\Delta\Pi$ (concentrate-permeate). The high sugar permeate from the final stage is recycled through a lower-concentration stage, from which permeate is rejected. Cheryan provides a process schematic on p. 456. Apple-juice concentration has received much attention, but commercial success has been elusive. Other membrane processes are widely used in the juice industry, but for concentration applications, high osmotic pressure and flavor leakage through the membrane are barriers to wider adoption. After many years only a few plants are in operation.

Whey concentration, both of whole whey and ultrafiltration permeate, is practiced successfully, but the solubility of lactose limits the practical concentration of whey to about 20 percent total solids, about a 4× concentration factor. (Membranes do not tolerate solids forming on their surface.) Nanofiltration is used to soften water and clean up streams where complete removal of monovalent ions is either unnecessary or undesirable. Because of the ionic character of most NF membranes, they reject polyvalent ions much more readily than monovalent ions. NF is used to treat "salt whey," the whey expressed after NaCl is added to curd. Nanofiltration permits the NaCl to permeate while retaining the other whey components, which may then be blended with ordinary whey. NF is also used to deacidify whey produced by the addition of HCl to milk in the production of casein.

Basic Principles of Operation RO and NF are pressure-driven processes where the solvent is forced through the membrane by pressure, and the undesired coproducts frequently pass through the membrane by diffusion. The major processes are rate processes, and the relative rates of solvent and solute passage determine the quality of the product. The general consensus is that the solution-diffusion mechanism describes the fundamental mechanism of RO membranes, but a minority disagrees. Fortunately, the equations presented below describe the observed phenomena and predict experimental outcomes regardless of mechanism.

Driving Force For RO and NF, Eq. (22-62) becomes:

$$J = \frac{\tau_w}{} (P_f - P_p) - (\Pi_f - \Pi_p) = \frac{\tau_w}{} (\Delta P - \Delta\Pi) \qquad (22\text{-}73)$$

where τ_w is the water permeability of the membrane, $m^2/Pa{\cdot}s$, and the subscripts f and p refer to feed and permeate. Π is the osmotic pressure, Pa. Since the thickness of the active layer z is almost never known, Eq. (22-73) is usually modified to the form

$$J = \left(\frac{1}{R_m + R_n \cdots}\right)(\Delta P - \Delta\Pi) \qquad (22\text{-}74)$$

where R_m is the membrane resistance, $Pa{\cdot}s/m$. Other resistance terms $(R_n \cdots)$ may be added, such as terms for fouling or compaction. Normally, the important terms are the inherent membrane resistance, the driving pressure P, and the osmotic pressure in the feed, Π. For a high rejection RO membrane, the back-pressure and pressure terms for the permeate are insignificant. For most work, the van't Hoff approximation for osmotic pressure gives an adequate estimate:

$$\Pi = \nu n_s RT \qquad (22\text{-}75)$$

where νn_s is the total concentration of ions, $kmol/m^3$ [Eq. (22-71)] and $R = 8.313\ kPa{\cdot}m^3/kmol{\cdot}K$. This equation should not be used for any unusually high concentration operation, or where accuracy is important.

Salt flux across a membrane is due to effects coupled to water transport, usually negligible, and diffusion across the membrane. Eq. (22-60) describes the basic diffusion equation for solute passage. It is independent of pressure, so as $\Delta P - \Delta\Pi \to 0$, rejection $\to 0$. This important factor is due to the kinetic nature of the separation. Salt passage through the membrane is concentration dependent. Water passage is dependent on $P - \Pi$. Therefore, when the membrane is operating near the osmotic pressure of the feed, the salt passage is not diluted by much permeate water.

The flux equation assumes constant temperature. As T rises, Π rises slowly, but around 25°C the viscosity of water drops enough to produce about a 3 percent rise in flux per °C.

Effects of Operating Variables Figure 22-63 shows trends in effects as various operating variables change in RO. Similar effects apply to NF.

RO and NF Membranes Nanofiltration membranes, sometimes called "loose RO," are more open than RO, and lie between reverse osmosis and ultrafiltration. This definition is not precise. NF membranes are usually negatively charged composite membranes. Donnan exclusion is an important rejection mechanism for charged membranes, and charged NF membranes reject polyvalent anions to a much greater degree than monovalent ions. They are usually tight enough to reject uncharged solutes heavier than a few hundred daltons and can, under ideal conditions, be highly retentive to lactose while passing most monovalent salts in a whey stream. Degrees of ion passage are strongly concentration dependent, with all rejections of charged ions dropping rapidly with increasing ionic strength. $MgSO_4$ rejection may remain high while NaCl rejection drops at around a few thousand ppm.

Methods of Production Modern RO and NF membranes are of two basic types. The more traditional is the asymmetric (skinned) membrane formed by the addition of a nonsolvent to a thin coating of homogeneous polymer solution. As solvent leaves the polymer solution and nonsolvent enters it, the surface polymer precipitates which alters the mechanism of solvent-nonsolvent interchange in the layers below. Thus the top layer, or skin, has a fundamentally different structure. Researchers have learned techniques for preparing membranes with widely differing properties, including some with excellent salt rejection properties. Membranes may be made either in flat sheet or fiber form using this technique. Strathmann [in Porter (ed.), op. cit., pp. 1–60] gives a complete summary.

The second major membrane type is a composite. Starting with a loose asymmetric membrane, usually a UF membrane, a coating is applied which is polymerized in situ to become the salt rejecting membrane. This process is used for most high-performance flat-sheet RO membranes, as well as for many commercial nanofiltration membranes. The chemistry of the leading RO membranes is known, but details on NF membranes are mostly proprietary. It may be inferred from published properties that various chemical approaches are utilized. Further information on composites may be found in Petersen [*J. Membrane Sci.*, **83,** 81–150 (1993)].

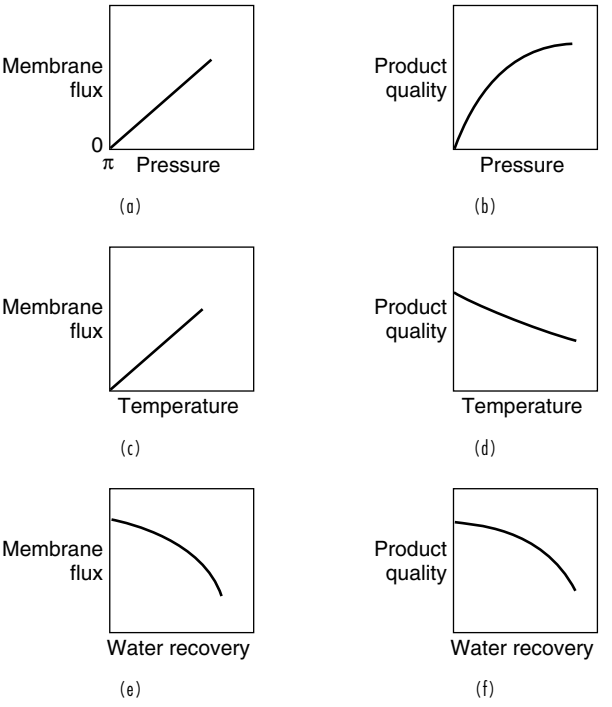


FIG. 22-63 Effects of operating variables on the performance of an RO membrane. (*a*) Water passage increases with pressure, assuming Π is constant. (*b*) Solute rejection rises with pressure, since solvent flux increases and solute diffusion does not. (*c*) Flux rises with temperature because viscosity declines. (*d*) Solute rejection declines with a temperature rise because of the osmotic pressure increase with temperature and because solute passage has a higher activation energy than does solvent passage. (*e*) Flux declines with increasing solute concentration, an osmotic-pressure effect. (*f*) At low-feed velocity past the membrane, solute is polarized at the membrane, while as velocity increases, mass transfer redisperses more of the polarized solute, lowering the effective solute concentration at the membrane. (Rejection is measured between permeate and bulk-feed concentration.) Bulk concentration of salt rises with recovery.

Membrane Characterization Membranes are always rated for flux and rejection. NaCl is always used as one measure of rejection, and for a very good RO membrane, it will be 99.7 percent or more. Nanofiltration membranes are also tested on a larger solute, commonly $MgSO_4$. Test results are very much a function of how the test is run, and membrane suppliers are usually specific on the test conditions. Salt concentration will be specified as some average of feed and exit concentration, but both are bulk values. Salt concentration at the membrane governs performance. Flux, pressure, membrane geometry, and cross-flow velocity all influence polarization and the other variables shown in Fig. 22-63.

Membrane Limitations Chemical attack, fouling, and compaction are prominent problems with RO and NF membranes. Compaction is the most straightforward. It is the result of creep, slow cold flow of the polymer resulting in a loss of water permeability. It is measured by the slope of log flux versus log time in seconds. It is independent of the flux units used and is reported as a slope, sometimes with the minus sign omitted. A slope of –0.001, typical for noncellulosic membranes, means that for every threefold increase in log(time), 10^3 seconds, a membrane looses 10 percent of its flux. Since membranes are rated assuming that the dramatic early decline in permeability has already occurred, the further decline after the first few weeks is very slow. Compaction is specific to pressure, temperature, and envi-

ronment.

Fouling is defined in "Background and Definitions" and is a significant problem in most process applications, and somewhat of a problem in most water applications. RO membranes may be fouled by sparingly soluble scalants which supersaturate at the membrane.

Chemical attack is often a result either of fouling prevention or cleaning in response to fouling. Chlorine and hypochlorite damage most RO and NF membranes, as do oxidants generally (see discussion of chlorine tolerance below).

Process Limitations

Osmotic Pressure In RO, and to a great extent NF, osmotic pressure is a critically important design consideration. A proper thermodynamic treatment of osmotic pressure may be found in Cheryan (op. cit., p. 13). Osmotic pressure is always calculated for the bulk-feed stream. It varies along the membrane train as salt concentration rises. The osmotic pressure that really matters is the one at the membrane, higher by the amount polarization raises the concentration there. As a general rule for a new membrane application, the inlet concentration is limited to about 0.5 N, for which $\Pi \approx 2.5$ MPa, giving a final concentrate Π of 5 MPa for 50 percent conversion. A few systems may be designed at much higher pressure, notably one of Du Pont's hollow fiber bundles, which is rated at 8 MPa. It is rated for 65 percent conversion on ocean water, and can concentrate sucrose to 60 percent using a special technique and membrane. Much of the appeal of NF membranes is their low-pressure operation.

Membrane Chemistry Three chemical families dominate the RO-NF membrane industry. Many other products are made on a small scale, and the field continues to attract significant R&D resources. But three types command most of the market.

Cellulose esters are the oldest. *Cellulose acetate* (CA) blend, a mixture of cellulose acetate (40.1 percent acetyl) and triacetate (43.2 percent acetyl) is the major polymer used; some cellulose triacetate and cellulose acetate-butyrate are used as well. Outstanding features of CA are its known behavior in many applications over many years, its slower fouling rate in some applications, its relative tolerance to chlorine, and foremost, its low cost. Where CA works well, there is little incentive to replace it by other materials. It has outstanding weaknesses including chemical and pH susceptibility, possible biodegradation, high compaction especially at elevated temperature, and poor rejection for organic solutes (due to their high solubility in CA). It is usually made as flat sheet, and occasionally as fibers.

Aromatic polyamide (aramid) membranes are a copolymer of 1-3 diaminobenzene with 1-3 and 1-4 benzenedicarboxylic acid chlorides. They are usually made into fine hollow fibers, 93 μm outer diameter by 43 μm inner diameter. Some flat sheet is made for spirals. These membranes are widely used for seawater desalination and to some extent for other process applications. The hollow fibers are capable of very high-pressure operation and have considerably greater hydrolytic resistance than does CA. Their packing density in hollow-fiber form makes them very susceptible to colloidal fouling (a permeator 8 inches in diameter contains 3 M fibers), and they have essentially no resistance to chlorine.

Cross-linked aromatic polyamides are the third major membrane type. The best known and most successful form has been an interfacially polymerized polyamide formed from 1-3 diaminobenzene and 1,3,5 benzenetricarboxylic acid chloride. This membrane is noted for excellent salt rejection and some degree of chemical resistance, including some resistance to chlorine, but it will not tolerate continuous exposure. The residual negative charge resulting from incomplete reaction and subsequent hydrolysis and ionization of the third acid-chloride group seems to help somewhat in improving its resistance to colloidal fouling. This membrane is made as flat sheet, and can be made in tubular form (13 mm inner diameter).

Chlorine Tolerance Most of the best RO membranes are attacked by oxidants, and they are particularly susceptible to chlorine. A particularly sensitive locus for attack is the amidic hydrogen. Cellulosic membranes are generally less sensitive, and pass the chlorine into the permeate giving downstream biocidal activity, very useful for under-the-sink RO. These factors are largely responsible for CA's survival in RO membranes. Chlorine, whatever its vices, has the virtue of being a known, effective, residual bactericide and a good inhibitor of bacterial growth on membranes (see fouling). It is also very useful in membrane cleaning, because not only does it kill bacteria, it breaks down some membrane deposits.

Chlorine is desirable as a bulk pretreatment biocide for inlet water, but its subsequent removal upstream of the membrane is absolutely necessary and difficult. $NaHSO_3$ is a common additive to dechlorinate before membranes. It is customarily added at 3–5 mg/l, an excess over the stoichiometric requirement. NH_3 is sometimes added to convert the chlorine to chloramine, a much less damaging biocide. Heavy metals present in seawater seem to amplify the damaging effects of chlorine and other oxidants.

Membranes are commonly rated for their chlorine tolerance in "ppm-hours," simply the product of the concentration and the contact time. Tolerance is temperature dependent.

Concentration Polarization Concentration polarization is a function of both flux, which increases the mass rate of material stranded at the membrane and cross-flow velocity, which reduces polarization by enhancing feed-side mass transfer. Polarization is far less of a problem in reverse osmosis and nanofiltration than it is in ultrafiltration or microfiltration, but it cannot be ignored. If cross-flow velocity is insufficient, rejected species concentrate near the membrane to an unacceptable level. The resulting increase in osmotic pressure and the precipitation of sparingly soluble species (scaling) are concerns. Scale inhibitors are normally added to water when they are appropriate and, for these feeds, careful consideration of cross-flow velocity is required. Hollow-fiber modules operate at low flux and at low cross-flow velocity so diffusion is better able to reduce polarization; spirals have much better redispersion rates, but can be overdriven if operated at fluxes above the design values. The equations for polarization are given below in the section describing ultrafiltration.

Rejection Rejection is defined in "Background and Definitions." The highest-rejection membranes are those designed for single-pass production of potable water from the sea. The generally accepted criterion is 99.4 percent rejection of NaCl. Some membranes, notably cellulose triacetate fibers are rated even higher. A whole range of membranes is available as rejection requirements ease, and membranes with excellent chlorine resistance and hydrolytic stability can be made with salt rejection over 90 percent.

Plugging Silt carried into a membrane module may deposit and plug it. Membrane configurations differ markedly in their ability to tolerate suspended solids, with fine hollow fibers fed shell-side being least tolerant, and large bore tubes fed tube-side being most tolerant. Membrane manufacturers use the *silt density index* (SDI) to show the tolerance of their wares for suspended solids. The SDI is an arbitrary test, used to determine the plugging propensity of an RO feed. A 0.45 μm microfiltration membrane, 47 mm in diameter, is used for the test. The feed to be tested is passed through the filter at 30 psi (206 kPa).

The time required for the first 100 ml to pass through the filter is recorded. That is defined as t_0. The flow is continued for 15 minutes, then the time required for an additional 100 ml to pass through the fitter is recorded. That is defined as t_{15}. If the flow has continued throughout the test, that is, the stream has not been reduced to dropwise flow, the SDI is defined as:

$$\text{SDI} = \frac{100(t_{15} - t_0)}{15(t_{15})} = 6.67\,\frac{(t_{15} - t_0)}{(t_{15})} \qquad (22\text{-}76)$$

If the flow becomes dropwise during the 15 minutes, the formula is instead:

$$\text{SDI} = \frac{100}{(\text{minutes until flow becomes dropwise})} \qquad (22\text{-}77)$$

Examples: (1) The first 100 ml required 11 seconds, and after 15 minutes of flow, an additional 100 ml required 95 seconds. The SDI would be 5.9 (2) The first 100 ml took 37 seconds, but the flow became dropwise after 4 minutes. The SDI would be 25.

Fouling Fouling is as inevitable as death and taxes. All membranes foul. Prevention and remediation of fouling are major economic and operating concerns in the design of a membrane facility. Scaling results from the precipitation of sparingly soluble species. Colloids deposit on the membrane in spite of cross-flow, and biofouling is

a problem for most feeds. Much can be done to increase the interval at which a membrane unit must be shut down and cleaned. The silt density index is a reasonable, if qualitative, guide to the degree to which colloidal fouling becomes a dominating problem. Biofouling is highly dependent on the feed-biota level and on nutrient levels. Reduction of biological load through pretreatment with chlorine or another biocide is a common practice, and on a pilot scale, microfiltration is being tried. Limited success has come from attempts to maintain anaerobic conditions in the feed. Research in biofouling prevention and remediation is an active area.

Pretreatment For most membrane applications, particularly for RO and NF, pretreatment of the feed is essential. If pretreatment is inadequate, success will be transient. For most applications, pretreatment is location specific. Well water is easier to treat than surface water and that is particularly true for sea wells. A reducing (anaerobic) environment is preferred. If heavy metals are present in the feed even in small amounts, they may catalyze membrane degradation. If surface sources are treated, chlorination followed by thorough dechlorination is required for high-performance membranes [Riley in Baker et al., op. cit., p. 5–29]. It is normal to adjust pH and add antiscalants to prevent deposition of carbonates and sulfates on the membrane. Iron can be a major problem, and equipment selection to avoid iron contamination is required. Freshly precipitated iron oxide fouls membranes and requires an expensive cleaning procedure to remove. Humic acid is another foulant, and if it is present, conventional flocculation and filtration are normally used to remove it. The same treatment is appropriate for other colloidal materials. Ultrafiltration or microfiltration are excellent pretreatments, but in general they are uneconomic.

Process Configuration

Osmotic Pinch Effect Feed is pumped into the membrane train, and as it flows through the membrane array, sensible pressure is lost due to friction effects. Simultaneously, as water permeates, leaving salts behind, osmotic pressure increases. There is no known practical alternative to having the lowest pressure and the highest salt concentration occur simultaneously at the exit of the train, the point where $\Delta P - \Delta\Pi$ is minimized. This point is known as the "osmotic pinch," and it is the point backward from which hydraulic design takes place. A corollary factor is that the permeate produced at the pinch is of the lowest quality anywhere in the array. Commonly, this permeate is below the required quality, so the usual practice is to design around average-permeate quality, not incremental quality. A 1 MPa overpressure at the pinch is preferred, but the minimum brine pressure tolerable is 1.1 times Π.

Brine Staging Velocity past the membrane is important. If too low, polarization is excessive, local Π rises, and rejection declines. Fouling occurs faster. If too high, pressure losses are higher than they need be, and the osmotic pinch is premature. Since the volume of feed declines continuously, the hydraulic design needs periodic rearrangement. This is commonly done as shown in Fig. 22-64, sometimes known as a Christmas tree. This design is commonly used where the fluid is pumped once, as in RO, NF, and gas-separation systems, but not where recirculation is practiced, as in ultrafiltration.

Economics The largest application for RO and NF is water treatment. Brackish water desalination for drinking water is the largest, and seawater desalination is perhaps the best known. Electrodialysis competes with pressure-driven membranes for brackish water applications. Seawater desalination is dominated by evaporation, with membranes an active competitor for midsize plants. There are numerous smaller process applications. The economic examples given are to illustrate the considerable difference between a small process plant and a large seawater RO plant. For the process plant, the cost given is for a skid-mounted self-contained unit for which considerable on-site additions would be required (tanks, piping, utilities, etc.). The seawater economics assume a leveled site but include everything necessary to deliver the product to the site boundary. Brackish water plants are considerably cheaper than seawater plants.

Process Applications The diversity of application for process RO permits only a few generalities. Sugar concentration, wastewater recovery, and beverage uses are a few of the currently popular applications. Taking a fairly standard 100 gpm (6.3 ℓ/s) (based on water permeated) system, a package unit (uninstalled) would cost approximately $90,000 (1995). Standard plant design uses 8-inch multileaf spiral modules. About 25 to 30 percent of the capital cost is for the membranes and housings. This is in line with costs for other membrane processes. Operating costs are predominantly for membrane replacement and power, each in the order of $80/1000 m^3 permeated. Approximately $25/1000 m^3 will be consumed for pretreatment, maintenance, and cleaning. Concentrate disposal costs are highly variable, and capital charges must be added. Spirals are the standard design for process plants, but tubes, plate and frame, and hollow fibers with boreside feed have market niches.

Seawater Desalination Seawater plants use spirals and hollow-fiber modules. Competition between these types is keen, with fibers having the advantage in high-salinity waters: polyamide fibers have higher pressure limits and cellulose triacetate fibers possess very high rejection. Spirals have an edge on cost, robustness, and fouling resistance. Seawater plant economics reflect the costs of high operating pressure, the need to handle and pretreat large quantities of seawater (2–2.5× rated capacity), and so on.

Capital Costs A typical medium-scale RO seawater plant might produce 0.25 m^3/s (6 MGD). For a plant with an open sea intake, seawater salinity of 38 g/l, and conversion of 45 percent, the overall cost would be $26.5 million (1996). A capital breakdown is given in Table 22-18. Capital charges are site specific, and are sensitive to the salinity of the feed. A plant of this size would likely contain six trains. For seawater RO, the best estimate for the slopes of the family of lines in Fig. 22-55 is –0.6 for the equipment and 0.95 for the membranes. Capital charges, shown in Table 22-19, usually dominate the overall economics; the numbers presented are only an example. Seawater economics are based on Shields and Moch, *Am. Desalination Assn. Conf. Monterey CA* (1996).

Operating Costs Annual operating costs for the example in Table 22-18 are shown in Table 22-19. For this 0.25 m^3/s plant, a service factor of 90 percent is assumed.

Energy For the plant described in Table 22-18, the energy consumption is given in Table 22-20. For any simple membrane plant, the power consumption is simply the feed pressure divided by the yield (P/Y) (Pa). Energy consumption is expressed as kWh/m^3, measured as net power fed to the plant divided by net permeate leaving the plant. Energy recovery can be very important in seawater plants, as shown here. Significant losses occur in motors, couplings, pumps, pipes, and

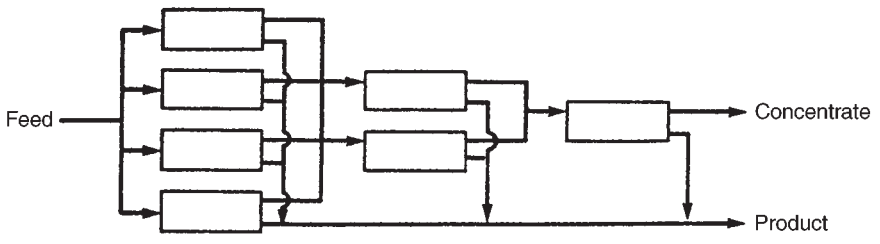


FIG. 22-64 Cascade arrangement for membrane processing to maintain cross-flow velocity as permeate is removed.

TABLE 22-18 RO Seawater Plant, Capital Costs

Item	$000	% of category	% of total capital
Membranes and housings, installed	3,600	21	14
Process equipment	13,700	79	52
Total installed equipment	17,300	100	65
Site development	500	21	2
Intake and outfall structures	1,850	79	7
Subtotal for site costs	2,350	100	9
Construction interest	983	14	4
Contingency	1,572	23	6
A&E fees	3,341	49	13
Working capital	983	14	4
Total indirect capital	6,879	100	26
Total capital employed	26,529		100

TABLE 22-19 RO Seawater Plant, Operating Costs

Item	$000	% of operating cost	% operating + capital	$/m^3 water
Electrical power @ $0.08/kWh	3,163	70	44	0.40
Consumables and chemicals	187	4	3	0.02
Maintenance and parts	482	11	7	0.06
Supervision and labor	265	6	4	0.03
Membrane replacement	390	9	5	0.05
Total	4,487	100	63	0.56
Amortization, 20 years, 8 percent	2,664		37	0.34
Total operating plus capital charges	7,151		100	0.90

manifolds.

ULTRAFILTRATION

Process Description *Ultrafiltration* (UF) is the membrane process which will retain soluble macromolecules and everything larger while passing solvent, ions, and other small soluble species. It is almost always operated with some means of forced convection near the membrane. Conventional dead-end filtration is rarely an option for UF, since most applications behave as if they have a "cake compressibility" factor of 1 in the filtration equation. Cross-flow filtration is practically universal for UF. An illustrative example of UF is its use for whey processing. Whey production exceeds 4×10^7 tons/year worldwide. It is a byproduct of cheese manufacture. Whey is composed of roughly 0.6 percent true proteins, 0.2 percent nonprotein nitrogen, 5 percent lactose, 1 percent salts, some lactic acid, and the balance water at a pH between 3.5 and 6. It contains trace amounts of casein fines and butterfat globules, and a large population of bacteria. UF retains the two principle proteins, alpha-lactalbumin (molar mass 17,000 daltons) and beta lactogloublin (molar mass 36,000 daltons), along with the large casein and butterfat particles and the bacteria. UF passes water, lactose, salts, and nonprotein nitrogen through the membrane into the permeate.

UF is widely used to concentrate oil-in-water emulsions, the byproduct of many metal-working applications, because the membrane retains stable emulsified oil while the water and the very low concentration of dissolved oil and free surfactant pass through it. UF is likewise useful for the concentration of dilute latex. Special membranes are used to remove virus from solution to help achieve the 12-log reduction required for vaccine manufacture. UF is useful for protein recovery in many fermentation operations, from the commodity-scale production of enzymes to small-scale specialty pharmaceutical manufacture.

TABLE 22-20 RO Seawater Plant, Energy Consumption

Item	kWh/m^3	% of total
Low-pressure pumps	0.70	14
High-pressure pumps	5.79	116
Energy recovery turbine	(1.94)	–39
Degasification	0.02	0
Product pump	0.16	3
Plant services	0.28	6
Total energy	5	100

Ultrafiltration may be distinguished from other membrane operations by example: When reverse osmosis is used to process whey, it passes only the water and some of the lactic acid (due to the solubility of lactic acid in RO membranes). Nanofiltration used on whey will pass most of the sodium salts while retaining the calcium salts and most of the lactose. Microfiltration will pass everything except the particulates and the bacteria.

UF Membranes Design of UF membranes prizes high retention, hydrolytic stability, and good process flux. Since fouling is the principal impediment to flux, and membranes which are hydrophilic generally foul less rapidly, there is competition between the truly stable hydrophobic membranes and the less-fouling-prone hydrophilic ones.

Cellulosic Membranes The first commercial UF membranes were made from *cellulose acetate* (CA), with an acetyl content of about 37 percent. They are prized for their low level of interaction with proteins and are still used in other applications where long life is not critical.

Polymeric Membranes Economically important applications required membranes that could operate at higher pH than could CA, for which the optimum is around pH = 5. Many polymeric membranes are now available, most of which have excellent hydrolytic stability. Particularly prominent are polysulfone, polyvinylidene fluoride, polyethersulfone, polyvinyl alcohol-polyethylene copolymers, and acrylic copolymers.

Ceramic Membranes Alumina-based microfiltration membranes and porous carbon substrates are tightened for use as UF membranes usually by depositing a layer of zirconium oxide on the surface.

UF Membranes as a Substrate for RO An important use of UF membranes is as a substrate for composite reverse-osmosis membranes. After the UF membrane (usually polysulfone) is prepared, it is coated with an aqueous solution of an amine, then dipped in an organic solution of an acid chloride to produce an interfacially polymerized membrane coating.

Membrane Characterization The two important characteristics of a UF membrane are its permeability and its retention characteristics. Ultrafiltration membranes contain pores too small to be tested by bubble point. Direct microscopic observation of the surface is difficult and unreliable. The pores, especially the smaller ones, usually close when samples are dried for the electron microscope. **Critical-point drying** of a membrane (replacing the water with a fluid which can be removed at its critical point) is utilized; even though this procedure has complications of its own it has been used to produce a few good pictures.

Water Flux The permeability of a UF membrane is determined by pore size, pore density, and the thickness of the membrane active layer. Water flux is measured in the absence of solute, generally on a newly made or freshly cleaned sample. The test is simple, and involves passing water through the membrane generally in dead-end flow under carefully controlled conditions. In a water flux test, the membrane behaves as a porous medium with the flow described by Darcy's law. Adjustments for viscosity and pressure are made to correct the results to standard conditions, typically the viscosity of water at 25°C and the pressure to 50 psi (343 kPa). The water flux will be many multiples of the process flux when the membrane is being used for a separation. Virgin membrane has a standard water flux of over 1 mm/sec. By the time the membrane is incorporated into a device and used in an application, that flux drops to perhaps 100 μm/s. Process fluxes are much lower.

Molecular Weight Cutoff The best-known method for characterizing UF membranes is molecular weight cutoff. Unfortunately, it is widely misunderstood and has been the source of much error. The concept of *molecular weight cutoff* (MWCO) is powerful and deceptively simple. Ultrafilters retain soluble molecules, so their retention is

measured by seeing which molecules will pass through them. The definition, generally *but not universally* followed is: molecular weight cutoff is the molar mass of the globular protein which is 90 percent retained by the membrane.

There are many complications with interpreting MWCO data. First, UF membranes have a distribution of pore sizes. In spite of decades of effort to narrow the distribution, most commercial membranes are not notably "sharp." What little is known about pore-size distribution in commercial UF membranes fits the Poisson distribution or log-normal distribution. Some pore-size distributions may be polydisperse.

Second, most membrane materials adsorb proteins. Worse, the adsorption is membrane-material specific and is dependent on concentration, pH, ionic strength, temperature, and so on. Adsorption has two consequences: it changes the membrane pore size because solutes are adsorbed near and in membrane pores; and it removes protein from the permeate by adsorption in addition to that removed by **sieving.** Porter (op. cit., p. 160) gives an illustrative table for adsorption of Cytochrome C on materials used for UF membranes, with values ranging from 1 to 25 percent. Because of the adsorption effects, membranes are characterized only when clean. Fouling has a dramatic effect on membrane retention, as is explained in its own section below.

Third, picking the point on the curve of retention versus molar mass where "90 percent" falls is inexact. The retention curve usually bends in a way that makes picking the "90 percent point" somewhat arbitrary.

Fourth, selection of the marker molecule can effect the MWCO measured. Markers for UF membranes are usually protein, but always polymeric. Polymers of the same molar mass can have very different molecular size, and MWCO is more a measure of size than anything else. To further complicate the picture, molecular shape can change in the vicinity of a membrane. One well-known example [Porter (ed.), op. cit., pp. 156–160] is Dextran 250, a branched polysaccharide with molar mass 250 kilodaltons which passes through a 50 kD MWCO membrane. Linear molecules, such as polyacrylic acid, with a given molecular mass passes easily through a membrane that retains a globular protein of the same molecular mass. The definition requires globular proteins, for which many of these effects are mitigated.

When testing a membrane using protein, in keeping with the definition of MWCO, it is necessary to keep the concentration in the feed and the flux very low to minimize polarization effects. Any polarization of the marker at the membrane will alter the measured value, and significant accumulation will result in **autofiltration.** The result is a measurement of the boundary layer rather than the membrane itself. What is needed are conditions in which J/k [see Eq. (22-91)] is close to 1. Reducing the marker concentration to minimize these problems raises the probability that adsorption will become important in reducing the concentration of marker in the permeate. A lack of reproducibility between laboratories is one manifestation of the intractability of the MWCO problem.

Membrane manufacturers require a standard test to maintain batch-to-batch quality. Few use proteins. Materials selected are ones for which the complications are minimized, the probe is simple, fast, and cheap to detect, does not readily biodegrade, and gives results, whatever they are, which are reproducible. There is no standardization of these tests within the industry.

Misunderstandings arise when membrane users assume that MWCO means what it seems to say. The definition implies that a 50 kD membrane will separate a 25 kD material from a 75 kD material. The rule of thumb is that the molecular mass must differ by a factor of ten for a good separation. Special techniques are used to permit the separation of proteins with much smaller mass ratio.

In an ideal world, membranes would contain a very high density of fully uniform, cylindrical pores. It is perhaps natural to envision a membrane as a uniform plane featuring cylindrical holes, challenged by rigid, spherical particles. None of these preconceptions is true. Membrane surfaces may be relatively rough, openings are neither uniform nor cylindrical, and are randomly spaced. A tiny minority of retained species are spherical and rigid; the vast majority is neither. It is perhaps instructive that in spite of the very creative effort invested in "sharp" membranes, their share of the overall membrane market is very small. Practically speaking, ordinary membranes have proven to be adequate for most separations. Very few membranes are used under conditions remotely approaching a test for MWCO. They are usually highly polarized with retention determined more by autofiltration than by inherent properties.

Autofiltration The retention of any material at the surface of the membrane gives rise to the possibility of a secondary or a dynamic membrane being formed. This is a significant problem for fractionation by ultrafiltration because microsolutes are partially retained by almost all retained macrosolutes. The degree of retention is quite case-specific. As a rule of thumb, higher pressure and more polarization results in more autofiltration. Autofiltration is particularly problematic in attempts to fractionate macromolecules.

Process Limitations

Concentration Polarization Throughput data from countless ultrafiltration experiments are shown in two characteristic curves. Figure 22-65 shows flux as a function pressure. Figure 22-66 shows flux as a function of the log of retentate concentration. Figure 22-65 is for a fixed solute concentration. At low transmembrane pressure, Region I, flux is governed by the rate at which solvent passes a porous material—Darcy's law. The magnitude of flux will approximate the water flux if viscosity is the same. Increase the pressure, and at first the flux responds. Soon, however, there is no response to pressure at all (Region III), and in some extreme cases there are reports of a negative response to pressure. This counterintuitive response to an increase in driving force has received considerable attention, and what is going on can be described by looking at the concentration of retained solute stranded at the membrane. It is a given that cross-flow ultrafiltration membrane processes operate at steady state. It isn't unusual for a process to operate for weeks or months at a flux essentially the same as that measured a few minutes after startup. It is therefore apparent that there is no long-term buildup of retained material at the membrane. Therefore, the redispersion of retained material must equal its rate of transport toward the membrane. Flux in the pressure-independent portion of Fig. 22-65 is quantitatively described by making a material balance on the retained solute, and solving the mass-transfer equations for its redispersal. These same equations describe the phenomenon shown in Fig. 22-66, flux at a constant stirring rate but with concentration as a variable.

Because this mass-transfer step is so vital, conventional dead-end operation of ultrafilters is very rare. There are many ways to depolarize a membrane. Cross-flow is by far the most common. Turbulent flow is more common than laminar flow.

The mass-transfer coefficient, k, is contained in the Sherwood number:

$$\mathrm{Sh} = \frac{kd_h}{D} \tag{22-78}$$

For turbulent flow, a correlation attributed to Chilton-Colburn is:

$$\mathrm{Sh} = 0.023\mathrm{Re}^{0.8}\mathrm{Sc}^{0.33} \tag{22-79}$$

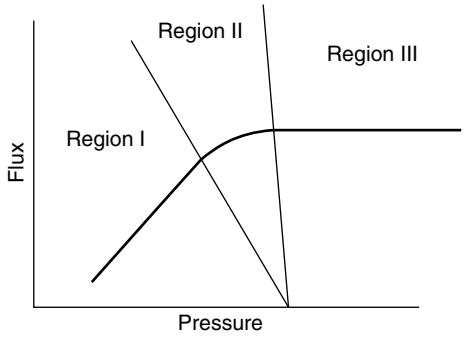


FIG. 22-65 Characteristic curve for flux as a function of pressure for cross-flow membrane processes limited by mass transfer at the membrane.

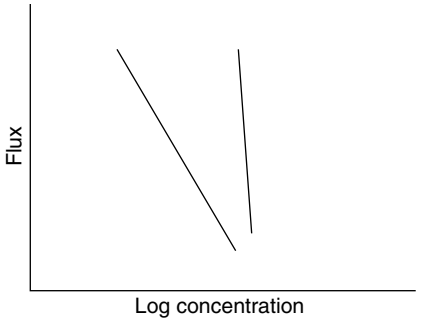


FIG. 22-66 Characteristic curve for flux as a function of feed composition for cross-flow membrane. Right curve is for a higher Sherwood number than the left curve.

$$\mathrm{Sc} = \frac{\nu}{D} \tag{22-80}$$

$$\mathrm{Re} = \frac{Vd}{\nu} \tag{22-81}$$

D is diffusivity, m^2/s, d_h is hydraulic diameter, (4)(cross sectional area)/(wetted perimeter), m, k is the mass-transfer coefficient, m/s, V is the velocity, m/s, and ν is the kinematic viscosity, m^2/s.

For cylindrical flow channels, $d_h = d$, and Re expressed in terms of volumetric flow rate, Q, is:

$$\mathrm{Re} = 4Q/\pi\nu d \tag{22-82}$$

where Q is in m^3/s. Defining J as acting along the x axis, passing from the feed through the membrane into the permeate, and recalling the steady-state stipulation, from Eq. (22-59), the rate of redispersion of retained material from the membrane is:

$$J_{\text{solute}} \approx -N_{\text{solute}} = D\frac{dC}{dx} \tag{22-83}$$

where x is the distance normal to the membrane.

A material balance on solute, ignoring the effects parallel to the membrane, is:

$$J \cdot C_x - J \cdot C_{\text{perm}} - D\frac{dC}{dx} = 0 \tag{22-84}$$

Calling the thickness of the concentration boundary layer, δ, Eq. (22-84) can be integrated to give:

$$J_{\text{solute}} \sim \left(\frac{D}{\delta}\right)\ln\left(\frac{C_{\text{wall}} - C_{\text{perm}}}{C_{\text{bulk}} - C_{\text{perm}}}\right) = k\ln\left(\frac{C_{\text{wall}} - C_{\text{perm}}}{C_{\text{bulk}} - C_{\text{perm}}}\right) \tag{22-85}$$

Since D/δ is the mass-transfer coefficient. For the portion of the operating curve in which flux is invariant, the wall concentration is apparently invariant. The mechanism governing why and how that occurs is the subject of a continuing debate in the literature.

For the usual case when $R = 1$ (total retention of the solute), $C_{\text{perm}} = 0$ and combining these equations gives a general expression for flux in a turbulent-flow membrane system. For any given solute concentration:

$$J \sim J_{\text{solute}} \sim k \sim \frac{Q^{0.8}D^{0.7}}{d^{1.8}\nu^{0.5}} \tag{22-86}$$

Flux is a function of solute concentration as is shown in Fig. 22-66. The exponent on Q is not always found to be 0.8 experimentally.

For laminar flow in a circular tube, the Leveque relationship is:

$$\mathrm{Sh} = 1.62\left(\mathrm{ReSc}\,\frac{d}{l}\right)^{0.33} \tag{22-87}$$

$$k = 1.62\left(\frac{VD^2}{ld}\right)^{0.33} \tag{22-88}$$

$$J \sim J_{\text{solute}} \sim k \sim \left(\frac{QD^2}{ld^3}\right)^{0.33} \tag{22-89}$$

where l is the distance from the channel entrance.

Equations (22-86) and (22-89) are the turbulent- and laminar-flow flux equations for the pressure-independent portion of the ultrafiltration operating curve. They assume complete retention of solute. Appropriate values of diffusivity and kinematic viscosity are rarely known, so an a priori solution of the equations isn't usually possible. Interpolation, extrapolation, even prediction of an operating curve may be done from limited data. For turbulent flow over an unfouled membrane of a solution containing no particulates, the exponent on Q is usually 0.8. Fouling reduces the exponent and particulates can increase the exponent to a value as high as 2. These equations also apply to some cases of reverse osmosis and microfiltration. In the former, the constancy of C_{wall} may not be assumed, and in the latter, D is usually enhanced very significantly by the action of materials not in true solution.

Usually, diffusivity and kinematic viscosity are given properties of the feed. Geometry in an experiment is fixed, thus d and averaged l are constant. Even if values vary somewhat, their presence in the equations as factors with fractional exponents dampens their numerical change. For a continuous steady-state experiment, and even for a batch experiment over a short time, a very useful equation comes from taking the logarithm of either Eq. (22-86) or (22-89) then the partial derivative:

$$\left(\frac{\partial \log J}{\partial \log Q}\right)_{\nu,d,D} = m \tag{22-90}$$

Equation (22-90) is the basis for the ubiquitous plots of log J versus log Q. Such plots are powerful tools for analyzing experimental data. The known range of observed values of m in well-developed turbulent flow is $0.8 < m < 2.0$. For laminar flow, $m = 0.33$ for true solutions, with values up to around 0.8 for systems with particulates. It is important to determine the experimental value, both for design optimization and for prediction of long-term effects. It is important that all values of flux be taken in the pressure-independent region of operation (see Fig. 22-65). High values of m are usually found in systems containing large, dense particles. Polyvinyl chloride latex with particles over 0.5 μm diameter is a classic high-slope example.

The slope of the flux-flow line is an indicator of fouling. In turbulent flow, $m < 0.8$ indicates fouling. A decline in the value of m with time is the most sensitive indicator of fouling. While the slope is difficult to obtain unconfounded by changes in pressure, a well-designed J versus Q experiment yields results with good predictive value for fouling. As a special precaution when using spiral-wound modules Da Costa, Fane, and Wiley [*J. Membrane Sci.*, **87,** 79–98 (1994)] found that while the pressure-drop data in a spiral module behave as if the flow is turbulent, the mass-transfer data are consistent with laminar flow.

Prediction of C_{wall} Equation (22-85) shows a semilog dependency of wall concentration on flux. Experimentally, the dependence of flux on concentration usually deviates significantly from linearity well before the zero-flux intercept extrapolated from data in Fig. 22-66. Experimental data at very low flux are difficult to gather, but usually the flux is much higher than the values extrapolated assuming linearity. The mass-transfer equations predict a mass-transfer coefficient, k, without reference to flux, as they were formulated for nonmembrane systems. This k is used by assumption to predict the wall concentration up to the point at which flux becomes independent of pressure.

$$C_{\text{wall}} - C_{\text{perm}} = (C_{\text{bulk}} - C_{\text{perm}})\exp(J/k) \tag{22-91}$$

When flux becomes independent of pressure, C_{wall} becomes **constant.** The assumptions underlying the equations, such as constancy of D and especially of ν are unlikely to hold, and other means are needed to determine the true value of C_{wall}. Field [in Howell, Sanchez, and Field, op. cit., pp. 87–95] gives a detailed treatment of this regime.

Osmotic Pressure, Gel Effect, Etc. The reason for the apparent constancy of C_{wall} under usual operating conditions is still tentative.

For many years, it was thought that the macro solute forms a new phase near the membrane—that of a gel or gel-like layer. The model provided good correlations of experimental data and has been widely used. It does not fit known experimental facts. An explanation that fits the known data well is based on osmotic pressure. The van't Hoff equation [Eq. (22-75)] is hopelessly inadequate to predict the osmotic pressure of a macromolecular solution. Using the empirical expression

$$\Pi(C) = \sum_{n=1}^{n=3} a_i C^n \qquad (22\text{-}92)$$

where a_i are experimental constants it is possible to correlate experimental osmotic-pressure data for macro solutes and to predict the concentration at the membrane. Data now confirmed show osmotic pressures high enough to counter the transmembrane driving force [Jonsson, *Desalination,* **51,** 61–77 (1984)]. Other theories of the boundary layer exist, but they have not attracted adherents. In terms of predictive power, both the gel theory and the osmotic-pressure theory provide a framework for correlating data.

Fouling Everything fouls (Fig. 22-67), and in process UF fouling is a major concern. Because of its importance, industrial suppliers of membrane equipment place a major emphasis on understanding, controlling, and preventing fouling. Equipment and process conditions can be specified with confidence for most applications because of the extensive knowledge base accumulated in response to the problem.

Fouling is the term used to describe the loss of throughput of a membrane device as it becomes chemically or physically changed by the process fluid (often by a minor component or a contaminant). A manifestation of fouling in cross-flow UF is that the membrane becomes unresponsive to the hydrodynamic mass transfer which is rate-controlling for most UF. Fouling is different from concentration polarization. Both reduce output, and their resistances are additive. Raising the flow rate in a cross-flow UF will increase flux, as in Eq. (22-90). If the system is badly fouled, $m \sim 0$, and increasing or decreasing flow at constant pressure has little effect on flux. However, raising the pressure may raise flux. For an unfouled system in laminar flow $0.33 < m < 0.8$; for turbulent flow, $0.8 < m < 2$.

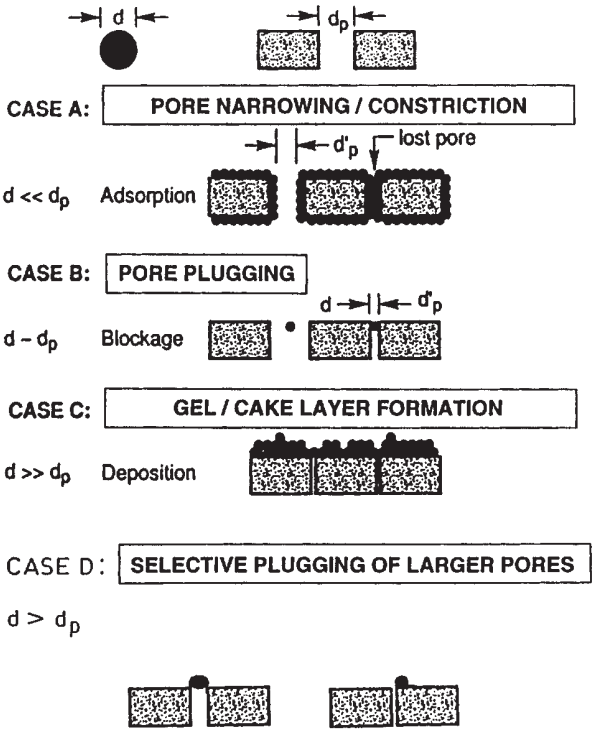


FIG. 22-67 Fouling schematics. Case A—Particles plug narrow pores and narrow larger ones. Case B—Particles plug narrow pores. Case C—Particles form a layer on the membrane. Case D—Particles or debris plug the largest pores. [*Courtesy Elsevier (modified).*]

Fouling affects flux dramatically. The pure water flux through a new UF membrane is commonly tenfold greater than the water flux after the membrane has been exposed to protein. Processing fluxes commonly decline roughly as $J = J_o t^{-n}$ where t is an arbitrary dimensionless time and n is small. J_o is the flux when $t = 1$. Thorough cleaning is required to restore $J = J_o$ as incompletely cleaned membranes foul faster than completely cleaned membranes. Fouling prevention is an important part of process design. Proper selection of membrane, operating conditions, feed pretreatment, startup techniques, and cleaning type and frequency can make a major difference in fouling, thus throughput, thus cost. There can be a startling difference between a well-designed process and a haphazard combination of membrane and process stream. Fouling also strongly influences retention.

Since flow through a porous membrane is always laminar, the volumetric flow through an individual pore is proportional to the fourth power of diameter, as known from the Pouiselle equation. Pore plugging, as in Case D, will dramatically lower flux and significantly increase retention, while Case B will have far less of an effect, lowering flux marginally and probably lowering retention. Even a slight reduction in pore diameter from an adsorption phenomenon (Case A) will have dramatic results. Some commercial membranes are designed with the inevitability of fouling in mind, and their behavior in the first minutes is inferior to their steady-state performance.

Cleaning membranes to restore their efficiency is normal in UF. Food and dairy systems require daily cleaning in any event for hygiene; more frequent cleaning is economically intolerable. A few industrial systems operate for six months between cleanings. Cleaning shortens membrane life, and it is often the major determinant of membrane-replacement frequency.

Among techniques to prevent fouling, pretreatment is widely practiced. Free-oil phases must be removed or stabilized, and whey processing benefits from holding the whey at a mildly elevated temperature for some minutes. Membranes operated at high transmembrane pressure foul much faster. The optimum operating point on Fig. 22-65 is Region II; however it is very difficult to design economical equipment to operate there. Pretreatment is often stream- or site-specific, and it has received little attention in the literature.

Some fouling occurs simply by contact, almost certainly due to adsorption. Some occurs slowly as material is processed, some of that due to trace components in the feed and some due to slow accumulation and rearrangement processes.

Process Configurations Ultrafiltration membranes are produced in four basic forms: tubular, hollow fiber/capillary, flat sheet, and ceramic monolith. Commercial diameter of tubes is 5 to 25 mm. Fibers range from a few mm down to 250 μm. Flat-sheet membrane is most common, made into spiral-wound modules, cassettes, and plate-and-frame devices. Spiral-wound flat sheet is by far the dominant commercial configuration, followed by capillaries in the millimeter range, and then 13 and 25 mm tubes. Spirals have the economic edge, and where they will work they are used. Tubes have the advantage of being tolerant of high solids loadings and of being extremely forgiving of process upsets. The finest fibers are only used for very clean feeds such as protein solutions and water.

The simplest ultrafiltration is the stirred cell, a batch operation. The most complex is a continuous stages-in-series operation incorporating diafiltration. Industrial practice incorporates the full gamut of complexity.

Process Objective UF is used for three principle objectives. First, to **fractionate,** to pass selectively one component through the membrane with the solvent. Second, to **concentrate,** to pass the solvent. These two, while different, are related and it is common to purify and concentrate a component simultaneously. The third objective, quite different, is to **produce a solvent stream** as a product. An example is the operation of an ultrafilter for producing low-cost permeate. An important application of UF is in the automotive industry where UF is used to remove water and microsolutes from huge electrophoretic paint tanks for use in rinsing excess paint (dragout) from

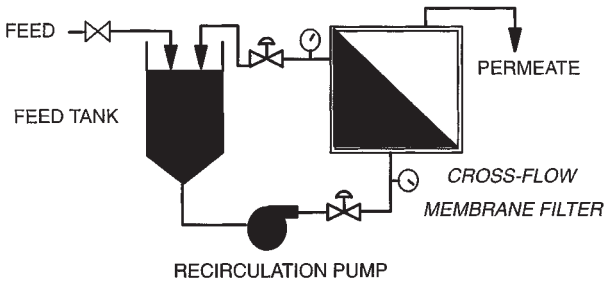


FIG. 22-68 Flow schematic for batch (feed valve closed) or semibatch (feed valve open) operation. (*Courtesy Koch Membrane Systems.*)

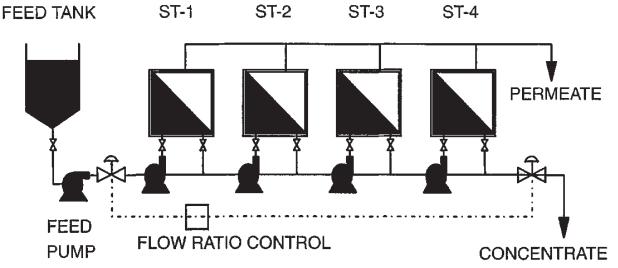


FIG. 22-69 Flow schematic for stages-in-series. In operation, the block valves are open. All pump inlets are connected, but in such a way as to prevent feed bypassing a stage. (*Courtesy Koch Membrane Systems.*)

newly primed auto bodies. Permeate and recovered paint are returned to the paint tank. It is undesirable to concentrate the paint, so the increase in paint solids within the UF loop is maintained below 10 percent.

Batch and Semibatch Straight batch is the least common industrial process, but semibatch is quite common (see Fig. 22-68). In **batch,** the entire quantity to be processed is put in a tank, and a feed from it is pumped across a UF membrane, with the concentrate returned to the tank. Conversion per pass is very low, but with recirculation any desired level of concentration may be obtained. It is the industrial version of the stirred cell. **Semibatch** uses a smaller tank to which fresh feed is introduced continuously. As the process proceeds, the contents of the batch tank become more concentrated with time, and at some point the feed is shut off and the tank contents are concentrated to the desired end point. Batch operation has the advantage of requiring the minimum membrane area, and the disadvantage of requiring the largest tank. Pumping costs are high because it is rarely practical to pressurize the feed tank or locate it at a height, so the circulating loop pressure is lost continuously.

For batch concentration, the yield equation is:

$$Y = \left(\frac{V_o}{V_f}\right)^{R-1} \tag{22-93}$$

Y is fractional yield of retained species, and V_o and V_f are the volume of process fluid at the beginning and end of a batch run, respectively. This equation is valid only when R, retention, is constant.

Diafiltration If a batch process is run so that the permeate is replaced by an equal volume of fresh solvent, unretained solutes are flushed through the system more efficiently. A major use of UF is fractionation, where a solvent, a retained solute and an unretained solute are present. An example is whey, containing water, protein, and lactose. If the retention of protein is 1 and the retention of lactose is 0, the concentration of protein in the retentate rises during UF. The ratio of protein to lactose rises, but the feed concentration of lactose is unchanged in retentate and permeate. Diafiltration dilutes the feed, and permits the concentration of lactose to be reduced. Diafiltration is used to produce high-purity products, and is used to fractionate high-value products. R is always <1 and >0 for every component.

For diafiltration, the yield equation is:

$$Y = \exp\left[\left(\frac{V_D}{V_o}\right)(R-1)\right] \tag{22-94}$$

where V_D is the volume of diafiltration solvent (water) added, equal to the volume of permeate removed.

The combination of diafiltration and batch concentration can be used to fractionate two macrosolutes whose retentions differ by as little as 0.2. It is possible *in principle* to achieve separations that are competitive with chromatography. When tanks and other equipment are considered, as well as the floor space they occupy, the economics of membrane separation of proteins may be attractive [R. van Reis, U.S. Patent 5,256,294 (1993)].

Stages in Series Large-scale UF normally operates in a mode called **stages-in-series** (see Fig. 22-69). Feed is pumped from a feed tank, which in principle can be quite small, to a first recirculating stage. A pipe connects the low-pressure side of this stage to the low-pressure side of another stage. When more than five stages are linked in this manner, the membrane area required drops to within 20 percent of the minimum batch membrane area requirement. The system is self-adjusting and stable. The preferred means of control is to use a volume-ratio controller to regulate the product-exit valve on the last stage. The economic advantages from modular fabrication, reduced tankage, and continuous operation make this the scheme of choice for most large fractionation and concentration operations.

Economic Yield Both in a high-value protein separation and in a low-value commodity concentration, economic yield is vital. Economic yield is defined as the fraction of useful product entering the process that leaves it in salable form. The yield equations used in the industry focus on retention, so they deal only with direct losses through the membrane. These losses result both in direct (product not sold) and indirect costs from a waste stream whose disposal or subsequent use may be more expensive when it is contaminated by macrosolute. There are additional indirect losses, mainly product left in the equipment, particularly that left adhering to the membrane. Costs of cleaning and disposal of this indirect loss, while hard to measure, are usually higher than the cost of product lost through the membrane.

Decoupled Driving Force and Depolarization Needs for improved fractionation motivate designers to reduce autofiltration. Using fluid velocity for depolarization means that hydrodynamic pressure drop will be additive to the transmembrane pressure driving force. Schemes to limit this effect confront a harsh economic reality. Two novel schemes decouple the driving from the depolarizing force.

When fluid flows around a curve in a duct, or when fluid is confined between differentially rotating cylinders, secondary flows called **Taylor vortices** are generated. If a membrane is mounted on a rotating cylinder, these secondary flows minimize polarization independent of driving pressure. The relevant equations are:

$$\mathrm{Ta} = \frac{\omega R g}{\nu}\sqrt{\frac{g}{R}} \tag{22-95}$$

$$\mathrm{Sh} = c\ \mathrm{Ta}^{0.5}\mathrm{Sc}^{0.33} \tag{22-96}$$

where c is an experimental constant, R is the radius of the inner cylinder, g is the gap between inner and outer cylinders, and ω is the angular velocity of the rotating cylinder, radian/s. Ta is the Taylor number. For a fixed device on a given fluid, flux is predicted to be proportional to $\omega^{1/2}$.

By mounting a plate-and-frame membrane assembly atop a torsion-bar spring, membranes may be depolarized by vibrating the stack at a resonant frequency. The membrane moves and the fluid is essentially stationary. At first thought to be ideal for, and limited to, solutions of very high viscosity or solids loading, the devices are now viewed as another economic competitor for a broader range of applications. No adequate theory is available to explain mass transfer in vibrating membrane systems. Some data correlate depolarizing mass transfer with the first power of shear rate over a narrow range of conditions.

Energy Requirements Practically all the energy needed to run an ultrafilter is depolarization energy. The thermodynamic work

required for any UF separation is approximately 0.01 kWh/m^3 of permeate. Energy requirements vary widely by application and economics. Design is a classic trade-off between membrane area and pump related equipment. The range of energy requirements from the easiest to the most difficult for modern designs runs in the magnitude of 0.5 to 5 kWh/m^3 of permeate.

Design UF equipment has considerable variety of design, but the trend is toward more compact, energy efficient, and lower-cost designs. Much of the robustness characteristic of older designs is now available in less costly versions.

Hydraulic Design Looking over a wide spectrum of UF applications, the hydraulic energy delivered to the membrane falls within a characteristic range. At the high extreme, a large-diameter tubular plant operating at very high velocity in order to retard fouling on a stream where long operating cycles between cleanings are valued, power dissipation at the membrane may exceed 150 watts/m^2. A well-designed, relatively large, hydraulically efficient plant will deliver power from electrical source to membrane at 64 percent efficiency. If the flux in the installation is 50 ℓmh, the power consumption of the process is 150/(0.64)(50) = 4.7 kWh/m^3. A large plant designed using less-efficient sanitary standard pumps and spiral-wound membranes could deliver 20 watts/m^2 to the membrane with an energy conversion of 50 percent and a flux of 30 ℓmh. That plant would consume 1.3 kWh/m^3. Very efficient plants for benign feed streams may consume half as much energy.

Module Types Favored Because of their low cost, spiral-wound membranes are the first choice for industrial ultrafiltration. Over the years, the number of applications for which spirals are a good choice has gone from practically none to over 50 percent, owing to very intensive process development and a related extensive modification of the spiral module as it was known in the RO field. When the spiral is not appropriate—examples include feeds where fibers, debris, certain types and loadings of suspended solids, most emulsified oils, etc. are present and too expensive to remove by pretreatment—other module designs are used. Capillary membranes are the usual next choice, and they are in fact preferred for some applications. Then comes open tubes, known for being expensive and practically indestructible. Tubes also have an edge in a few applications, such as apple juice, because they are able to recover more juice before they plug up with pommace. Cassettes are used because of direct scale-up from bench to plant in applications where equipment and operating cost are not paramount. Plate-and-frame modules are still found on occasion.

Economics The general examples section found under "Background and Definitions" is directly applicable to the following.

Capital Costs Package UF units are sold for many applications. Prices vary widely by application, with equipment designed for food and pharmaceutical applications priced higher than general industrial equipment. All package units would include membranes, one or more pumps, a cleaning system, piping, instrumentation, an electrical control panel, and perhaps a process tank, all designed for rapid field installation. A 1996 budget price for a typical industrial spiral or capillary unit containing 100 m^2 of active membrane area, with a process output of the magnitude of 1.0–1.5 ℓ/s is $250–500/m^2. The replaceable membrane component of that cost is $30–40/m^2.

UF/MF applications with plant cost of $10^6 are considered large. In the decade ending in 1995, fewer than ten large plants were sold worldwide in any year. During that decade, the process-membrane industry matured. More vendors for equipment and membranes broadened the applications and lowered the costs. The industry-cost picture is changing fast enough that only broad guidelines are given here. Fresh information from vendors and users is needed if accuracy is required.

UF and MF use energy to depolarize membranes so as to increase flux. As is shown in Fig. 22-55, membranes and mechanical equipment are traded off to achieve an overall economic minimum. Three things can drive a design toward the use of more membranes and less mechanical equipment: cheaper membranes, very high flux, and very low flux. The availability of lower-cost membranes is easiest to understand. In the five years ending in 1995, the cost of both membrane area and membrane housings was driven down by competition. Pumps, pipes, and other peripheral equipment also declined, but not as much. By the principles of Fig. 22-55, this pushed the optimum design point to the right. Membrane costs maintained their *slope* but came down in *position.* Neither high-flux applications (potable water for example, average design flux for UF is 125 ℓmh, and for MF it is 185 ℓmh) or very low flux (polyvinylalcohol, average design flux 5.8 ℓmh) are very responsive to mechanical energy applied at the membrane. In the case of water, there is little to depolarize, and most systems operate in Region I of Fig. 22-13. Polyvinylalcohol is so viscous that it is, or becomes, laminar in a spiral module. The pressure drop through a spiral limits the velocity and forces the economics toward plants with high-area and moderate-pumping packages.

In the case of whey, paint, and other midflux process fluids, mechanical energy at the membrane surface produces a larger dividend. For these applications, pumping for depolarization is much more important economically, but the trend toward lower-cost membranes has nonetheless shifted systems toward more membrane area.

TABLE 22-21 Capital-Cost Distribution for Components in Large UF/MF Plants

Cost distribution	% of total, range
Membranes and membrane housings	17–40
Pumps, motors, etc.	15–9
Pipes, valves, and framework	35–31
Cleaning system	18–10
Control panel	15–10

In 1996, a $1M plant would process: 6 ℓ/s of polyvinylalcohol (UF), 17 ℓ/s of whey (UF), 35 ℓ/s dextrose (MF), or 108 ℓ/s water (MF or UF).

During 1990–1995, capital costs for large UF/MF plants broke down into the ranges shown in Table 22-21.

Operating Costs Operating expenses again span a considerable range, but there are fairly consistent operating norms (Table 22-22). A few very high flux MF applications with fluxes of up to 500 ℓmh are just starting to become commercial. These applications use large pumps to maintain output. It is not yet know whether these cost estimates will apply to those plants.

TABLE 22-22 Operating-Cost Range for Large UF/MF Plants

Expense item	Range of variable commonly encountered
Energy consumption	0.5–5 kWh/m^3 permeated
Cleaning chemicals and lost product	$10–100/m^2 membrane installed-year
Membrane replacement	1–5 years at $20–40 m^2; 10–20 years at $200/m^2
Operating, cleaning, and maintenance labor	2–3% of installed capital
Maintenance materials	0.6–0.06% of installed capital

MICROFILTRATION

Process Description Microfiltration (MF) separates particles from true solutions, be they liquid or gas phase. Alone among the membrane processes, microfiltration may be accomplished without the use of a membrane. The usual materials retained by a microfiltration membrane range in size from several μm down to 0.2 μm. At the low end of this spectrum, very large soluble macromolecules are retained by a microfilter. Bacteria and other microorganisms are a particularly important class of particles retained by MF membranes. Among membrane processes, dead-end filtration is uniquely common to MF, but cross-flow configurations are often used.

Brief Examples Microfiltration is the oldest and largest membrane field. It was important economically when other disciplines were struggling for acceptance, yet because of its incredible diversity and lack of large applications, it is the most difficult to categorize. Nonetheless, it has had greater membrane sales than all other membrane applications combined throughout most of its history. The early

success of microfiltration was linked to an ability to separate microorganisms from water, both as a way to detect their presence, and as a means to remove them. Both of these applications remain important.

Laboratory Microfiltration membranes have countless laboratory uses, such as recovering biomass, measuring particulates in water, clarifying and sterilizing protein solutions, and so on. There are countless examples for both general chemistry and biology, especially for analytical procedures. Most of these applications are run in dead-end flow, with the membrane replacing a more conventional medium such as filter paper.

Medical MF membranes provide a convenient, reliable means to sterilize fluids without heat. Membranes are used to filter injectable fluids during manufacture. Sometimes they are inserted into the tube leading to a patient's vein.

Process Membrane microfiltration competes with conventional filtration, particularly with diatomaceous earth filtration in general-process applications. A significant advantage for membrane MF is the absence of a diatomaceous earth residue for disposal. Membranes have captured most of the final filtration of wine (displacing asbestos), are gaining market share in the filtration of gelatin and corn syrup (displacing diatomaceous earth), are employed for some of the cold pasteurization of beer, and have begun to be used in the pasteurization of milk. Wine and beer filtration operate dead-end; gelatin, corn syrup, and milk are cross-flow operations. MF is used to filter all fluid reactants in the manufacture of microcircuits to ensure the absence of particulates, with point-of-use filters particularly common.

Gas Phase Microfiltration plays an important and unique role in filtering gases and vapors. One important example is maintaining sterility in tank vents, where incoming air passes through a microfilter tight enough to retain any microorganisms, spores, or viruses. A related application is the containment of biological activity in purge gases from fermentation. An unrelated application is the filtration of gases, even highly reactive ones, in microelectronics fabrication to prevent particulates from contaminating a chip.

Downstream Processing Microfiltration plays a significant role in downstream processing of fermentation products in the pharmaceutical and bioprocessing industry. Examples are clarification of fermentation broths, sterile filtration, cell recycle in continuous fermentation, harvesting mammalian cells, cell washing, mycelia recovery, lysate recovery, enzyme purification, vaccines, and so forth.

MF Membranes Microfiltration is a mature field that has proliferated and subdivided. The scope and variety of MF membranes far exceeds that in any other field. A good overview is given by Strathmann [in Porter (ed.), op. cit., pp. 1–78]. MF membranes may be classified into those with tortuous pores or those with capillary pores. Tortuous-pore membranes are far more common, and are spongelike structures. The pore openings in MF are much larger than those in any other membrane. Surface pores may be observed by electron microscope, but tortuous pores are much more difficult to observe directly. Membranes may be tested by bubble-point techniques. Many materials not yet useful for tighter membranes are made into excellent MF membranes. Retention is the primary attribute of an MF membrane, but important as well are permeability, chemical and temperature resistance, dirt capacity (for dead-end filters), FDA-USP approval, inherent strength, adsorption properties, wetting behavior, and service life.

Membrane-production techniques listed below are applicable primarily or only to MF membranes. In addition, the Loeb-Sourirjain process, used extensively for reverse osmosis and ultrafiltration membranes, is used for some MF membranes.

Membranes from Solids Membranes may be made from microparticles by sintering or agglomeration. The pores are formed from the interstices between the solid particles. The simplest of this class of membrane is formed by sintering metal, metal oxide, graphite, ceramic, or polymer. Silver, tungsten, stainless steel, glass, several ceramics, and other materials are made into commercial membranes. Sintered metal may be coated by TiO_2 or zirconium oxide to produce MF and UF membranes. Membranes may be made by the careful winding of microfibers or wires.

Ceramic Ceramic membranes are made generally by the sol-gel process, the successive deposition of ever smaller ceramic precursor spheres, followed by firing to form multitube monoliths. The diameter of the individual channels is commonly about 2 to 6 mm. Monoliths come in a variety of shapes and sizes. A 19-channel design is common. One manufacturer makes large monoliths with square channels.

Track-Etched Track-etched membranes (Fig. 22-70) are now made by exposing a thin polymer film to a collimated beam of radiation strong enough to break chemical bonds in the polymer chains. The film is then etched in a bath which selectively attacks the damaged polymer. The technique produces a film with photogenic pores, whose diameter may be varied by the intensity of the etching step. Commercially available membranes have a narrow pore size distribution and are reportedly resistant to plugging. The membranes have low flux, because it is impossible to achieve high pore density without sacrificing uniformity of diameter.

Chemical Phase Inversion Symmetrical phase-inversion membranes (Fig. 22-71) remain the most important commercial MF membranes produced. The process produces tortuous-flow membranes. It involves preparing a concentrated solution of a polymer in a solvent. The solution is spread into a thin film, then precipitated through the slow addition of a nonsolvent, usually water, sometimes from the vapor phase. The technique is impressively versatile, capable of producing fairly uniform membranes whose pore size may be varied within broad limits.

Thermal Phase Inversion Thermal phase inversion is a technique which may be used to produce large quantities of MF membrane economically. A solution of polymer in poor solvent is prepared at an elevated temperature. After being formed into its final shape, a sudden drop in solution temperature causes the polymer to precipitate. The solvent is then washed out. Membranes may be spun at high rates using this technique.

Stretched Polymers MF membranes may be made by stretching

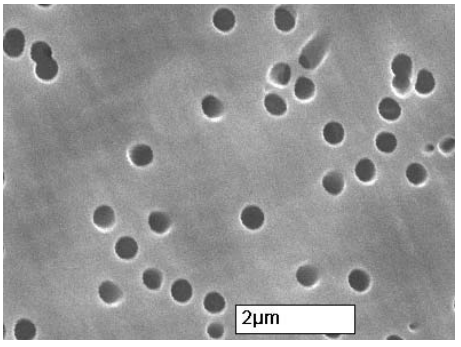


FIG. 22-70 Track-etched 0.4 μm polycarbonate membrane. (*Courtesy Millipore Corporation.*)

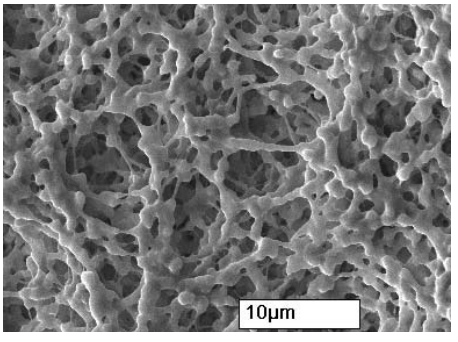


FIG. 22-71 Chemical phase inversion 0.45 μm polyvinylidene fluoride membrane. (*Courtesy Millipore Corporation.*)

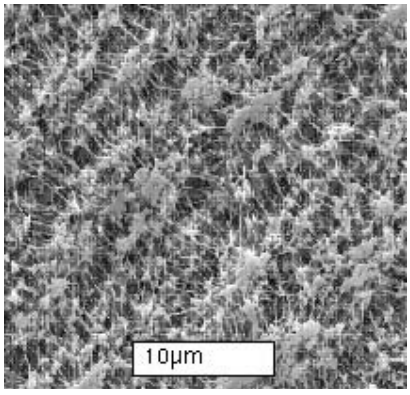


FIG. 22-72 Stretched polytetrafluoroethylene membrane. (*Courtesy Millipore Corporation.*)

(Fig. 22-72). Semicrystalline polymers, if stretched perpendicular to the axis of crystallite orientation, may fracture in such a way as to make reproducible microchannels. Best known are Goretex® produced from Teflon®, and Celgard® produced from polyolefin. Stretched polymers have unusually large fractions of open space, giving them very high fluxes in the microfiltration of gases, for example. Most such materials are very hydrophobic.

Membrane Characterization MF membranes are rated by flux and pore size. Microfiltration membranes are uniquely testable by direct examination, but since the number of pores that may be observed directly by microscope is so small, microscopic pore size determination is mainly useful for membrane research and verification of other pore-size-determining methods. Furthermore, the most critical dimension may not be observable from the surface. Few MF membranes have neat, cylindrical pores. Indirect means of measurement are generally superior. Accurate characterization of MF membranes is a continuing research topic for which interested parties should consult the current literature.

Bubble Point Large areas of microfiltration membrane can be tested and verified by a bubble test. Pores of the membrane are filled with liquid, then a gas is forced against the face of the membrane. The Young-Laplace equation, $\Delta P = (4\gamma \cos \Theta)/d$, relates the pressure required to force a bubble through a pore to its radius, and the interfacial surface tension between the penetrating gas and the liquid in the membrane pore. γ is the surface tension (N/m), d is the pore diameter (m), and P is transmembrane pressure (Pa). Θ is the liquid-solid contact angle. For a fluid wetting the membrane perfectly, $\cos \Theta = 1$.

By raising the gas pressure on a wet membrane until the first bubble appears, the largest pore may be identified, and its size computed. This is a good test to run on a membrane apparatus used to sterilize a fluid, since bacteria larger than the identified largest pore (or leak) cannot readily penetrate the assembly. Pore-size distribution may also be run by bubble point. Bubble-point testing is particularly useful in assembled microfilters, since the membrane and all seals may be verified. Periodic testing insures that the assembly retains its integrity. Diffusional flow of gas is a complication in large MF assemblies. It results from gas dissolving in pore liquid at the high-pressure side, and desorbing at the low-pressure side If the number of pores and the average pore length are known, the effect can be computed. Special protocols are used when this method is used for critical applications. Detail is provided in ASTM F316-86, "Standard test method for pore size characteristics of membrane filters by bubble point and mean flow pore test." The bubble-point test may also be run using two liquids. Because interfacial surface tensions of liquids can be quite low, this technique permits measurements on pores as small as 10 nm.

Charged Membranes The use of tortuous-flow membranes containing a positive electrical charge may reduce the quantity of negatively charged particles passing even when the pore size is much larger than the particle. The technique is useful for making prefilters or layered membranes that withstand much higher solids loadings before becoming plugged.

Bacteria Challenge Membranes are further tested by challenge with microorganisms of known size: their ability to retain all of the organisms is taken as proof that all pores are smaller than the organism. The best-known microorganism for pore-size determination is *Pseudomonas diminuta,* an asporogenous gram-negative rod with a mean diameter of 0.3 µm. Membranes with pore size smaller than that are used to ensure sterility in many applications. Leahy and Sullivan [*Pharmaceutical Technology,* **2**(11), 65 (1978)] provide details of this validation procedure.

Membrane thickness is a factor in microbial retention. Tortuous-pore membranes rated at 0.22 µm typically have surface openings as large as 1 µm (Fig. 22-71). Narrower restrictions are found beneath the surface. In challenge tests, *P. diminuta* organisms are found well beneath the surface of an 0.2 µm membrane, but not in the permeate.

Latex Latex particles of known size are available as standards. They are useful to challenge MF membranes.

Process Configuration As befits a field with a vast number of important applications and a history of innovation, there are countless variations on how an MF process is run.

Dead-end versus Cross-flow Conventional filtration is usually run dead-end, and is facilitated by amendments that capture the particulates being removed. Membranes have very low dirt capacity, so only applications with very low solids to be removed are run in conventional dead-end flow. A rough upper limit to solids content is about 0.5 percent; streams containing <0.1 percent are almost always processed by dead-end devices. Since dead-end membrane equipment is much less expensive than cross-flow, great ingenuity is applied to protecting the critical membrane pores by structured prefilters to remove larger particles and debris. The feed may also be pretreated. It is common practice to dispose of the spent membrane rather than clean it. The membrane may be run inverted. A review of dead-end membrane filtration is given by Davis and Grant [in Ho and Sirkar (eds.), op. cit., pp. 461–479].

Cross-flow is the usual case where cake compressibility is a problem. Cross-flow microfiltration is much the same as cross-flow ultrafiltration in principle. In practice, the devices are often different. As with UF, spiral-wound membranes provide the most economical configuration for many large-scale installations. However, capillary devices and cassettes are widely employed, especially at smaller scale. A detailed description of cross-flow microfiltration had been given by Murkes and Carlsson [*Crossflow Filtration,* Wiley, NY (1988)].

Membrane Inverted Most membranes have larger openings on one face than on the other. Common practice is to run the tightest face against the feed in order to avoid plugging of the backing by particles. The rationale is that anything that makes it past the "skin" will have relatively unimpeded passage into the backing and out with the permeate. For very low solids this convention is reversed, the rationale being that the porous backing provides a trap for particulates, rather like filter aid.

If the complete passage of soluble macromolecules is required, a highly polarized membrane is an advantage. The upside-down membrane hinders the back diffusion of macrosolutes. Countering the tendency of the retained particulates to "autofilter" soluble macrosolutes, the inhibition of back diffusion raises the polarization and thus the passage of macrosolutes such as proteins. The particulates are physically retained by the membrane. Blinding and plugging can be controlled if the membrane is backwashed frequently. This technique has been demonstrated at high solids loadings in an application where high passage of soluble material is critical, the microfiltration of beer [Wenten, Rasmussen, and Jonsson, *North Am. Membrane Soc. Sixth Annual Meeting,* Breckenridge, CO (1994)].

Liquid Backpulse Solid membranes are backwashed by forcing permeate backward through the membrane. Frequent pulsing seems to be the key.

Air Backflush A configuration unique to microfiltration feeds the process stream on the shell side of a capillary module with the permeate exiting the tube side. The device is run as an intermittent dead-end filter. Every few minutes, the permeate side is pressurized with air. First displacing the liquid permeate, a blast of air pushed back-

ward through the membrane pushes off the layer of accumulated solids. The membrane skin contacts the process stream, and while being backwashed, the air simultaneously expands the capillary and membrane pores slightly. This momentary expansion facilitates the removal of imbedded particles.

Process Limitations The same sorts of process limitations affecting UF apply to MF. The following section will concentrate on the differences.

Concentration Polarization The equations governing cross-flow mass transfer are developed in the section describing ultrafiltration. The velocity, viscosity, density, and channel-height values are all similar to UF, but the diffusivity of large particles (MF) is orders-of-magnitude lower than the diffusivity of macromolecules (UF). It is thus quite surprising to find the fluxes of cross-flow MF processes to be similar to, and often higher than, UF fluxes. Two primary theories for the enhanced diffusion of particles in a shear field, the inertial-lift theory and the shear-induced theory, are explained by Davis [in Ho and Sirkar (eds.), op. cit., pp. 480–505], and Belfort, Davis, and Zydney [*J. Membrane. Sci.*, **96,** 1–58 (1994)]. While not clear-cut, shear-induced diffusion is quite large compared to Brownian diffusion except for those cases with very small particles or very low cross-flow velocity. The enhancement of mass transfer in turbulent-flow microfiltration, a major effect, remains completely empirical.

Fouling Fouling affects MF as it affects all membrane processes. One difference is that the fouling effect caused by deposition of a foulant in the pores or on the surface of the membrane can be confounded by a rearrangement or compression of the solids cake which may form on the membrane surface. Also, the high, open space found in tortuous-pore membranes makes them slower to foul and harder to clean.

Equipment Configuration Since the early days when membrane was available only in flat-sheet form, the variety of offerings of various geometry and fabricated filter component types has grown geometrically. An entire catalog is devoted just to list the devices incorporating membranes whose area ranges from less than 1 cm^2 up to 3 m^2. Microfiltration has grown to maturity selling these relatively small devices. Replacement rather than reuse has long been the custom in MF, and only with later growth of very large applications, such as water, sewage, and corn sweeteners, has long membrane life become an economic necessity on a large scale.

Conventional Designs Designs familiar from other unit operations are also used in microfiltration. Cartridge-filter housings may be fitted with pleated MF membrane making a high-area dead-end membrane filter. Plate-and-frame type devices are furnished with MF sheet stock, and are common in some applications. Capillary bundles with tube-side feed are used for cross-flow applications, and are occasionally used in dead-end flow. A few tubular membranes are used. Spiral-wound modules are becoming increasingly important for process applications where economics are paramount. Belt filters have been made using MF membrane.

Ceramics Ceramic microfilters for commercial applications are almost always employed as tube-side feed multitube monoliths. They are also available as flat sheet, single tubes, discs, and other forms primarily suited to lab use. They are used for a few high-temperature applications, in contact with solvents, and particularly at very high pH.

Cassettes *Cassette* is a term used to describe two different cross-flow membrane devices. The less-common design is a usually large stack of membrane separated by a spacer, with flow moving in parallel across the membrane sheets. This variant is sometimes referred to as a **flat spiral,** since there is some similarity in the way feed and permeate are handled. The more common cassette has long been popular in the pharmaceutical and biotechnical field. It too is a stack of flat-sheet membranes, but the membrane is usually connected so that the feed flows across the membrane elements in series to achieve higher conversion per pass. Their popularity stems from easy direct scale-up from laboratory to plant-scale equipment. Their limitation is that fluid management is inherently very limited and inefficient. Both types of cassette are very compact and capable of automated manufacture.

Representative Process Applications

Pharmaceutical Removal of suspended matter is a frequent application for MF. Processes may be either clarification, in which the main product is a clarified liquid, or solids recovery. Separating cells or their fragments from broth is the most common application. Clarification of the broth in preparation for product recovery is the usual objective, but the primary goal may be recovery of cells. Cross-flow microfiltration competes well with centrifugation, conventional filtration by rotary vacuum filter or filter press and decantation. MF delivers a cleaner permeate, an uncontaminated, concentrated cell product which may be washed in the process, and generally gives high yields. There is no filter-aid disposal problem. Microfiltration has higher capital costs than the other processes, although total cost may be lower. The recovery of penicillin is an example of a process for which cross-flow microfiltration is generally accepted.

Water and Wastewater Microfiltration is beginning to be applied to large-scale potable-water treatment. Its major advantage is positive removal of cryptosporidium and giardia cysts, and its major disadvantage is cost. MF is used in a few large sewage-treatment facilities, where its primary advantage is that it permits a major reduction in the physical size of the facility.

Chemical MF is used in several applications to recover caustic values from cleaning or processing streams. An example is the caustic solution used to clean dairy evaporators, which may be cleaned for reuse by passing it through a microfilter. Significant savings in caustic purchase and disposal costs provide the incentive. Acids are also recovered and reused. Ceramic microfilters are most commonly used in these applications.

Food and Dairy Microfiltration has many applications in the food and dairy industries. An innovative dairy application uses MF membranes to remove bacteria as a nonthermal means of disinfection for milk. A special flow apparatus maintains a carefully controlled transmembrane pressure as the milk flows across the membrane. The concentrate contains the bacteria and spores, as well as any fat. The concentrate may be heat sterilized and recombined with the sterile permeate. In another milk application, some success is reported in separating fat from milk or other dairy streams by cross-flow microfiltration instead of centrifugation. Transmembrane pressure must be kept very low to prevent fat penetration into the membrane. In the food industry, MF membranes are replacing diatomaceous earth filtration in the processing of gelatin. The gelatin is passed with the permeate, but the haze producing components are retained. UF may be used downstream to concentrate the gelatin.

Flow Schemes The outline of batch, semibatch, and stages-in-series is given in the section describing ultrafiltration. Diafiltration is also described there. All these techniques are common in MF, except for stages-in-series, used rarely. MF features uses of special techniques to control transmembrane pressure in some applications. An example is one vendor's device for the microfiltration of milk. In most devices the permeate simply leaves by the nearest exit, but for this application the permeate is pumped through the device in such a way as to duplicate the pressure drop in the concentrate side, thus maintaining a constant transmembrane-pressure driving force. In spite of the low-pressure driving force, the flux is extremely high.

Limitations Some applications which seem ideal for MF, for example the clarification of apple juice, are done with UF instead. The reason is the presence of deformable solids which easily plug and blind an MF membrane. The pores of an ultrafiltration membrane are so small that this plugging does not occur, and high fluxes are maintained. UF can be used because there is no soluble macromolecule in the juice that is desired in the filtrate. There are a few other significant applications where MF seems obvious, but is not used because of deformable particle plugging.

Economics Microfiltration may be the triumph of the Lilliputians; nonetheless, there are a few large-industrial applications. Dextrose plants are very large, and as membrane filtration displaces the precoat filters now standard in the industry, very large membrane microfiltration equipment will be built.

Site Size Most MF processes require a smaller footprint than competing processes. Reduction in total-area requirements are sometimes a decisive economic advantage for MF. It may be apparent that

the floor-space costs in a pharmaceutical facility are high, but municipal facilities for water and sewage treatment are often located on expensive real estate, giving MF an opportunity despite its higher costs otherwise.

Large Plants The economics of microfiltration units costing about 10^6 is treated under ultrafiltration. When ceramic membranes are used, the cost optimum may shift energy consumption upward to as much as 10 kWh/m^3.

Disposables For smaller MF applications, short membrane life is a traditional characteristic. In these applications, costs are dominated by the disposables, and an important characteristic of equipment design is the ease, economy, and safety of membrane replacement.

Hygiene and Regulation Almost unique to MF is the influence of regulatory concerns in selection and implementation of a suitable microfilter. Since MF is heavily involved with industries regulated by the Food and Drug Administration, concerns about process stability, consistency of manufacture, virus reduction, pathogen control, and material safety loom far larger than is usually found in other membrane separations.

GAS-SEPARATION MEMBRANES

Process Description Gas-separation membranes separate gases from other gases. Some gas filters, which remove liquids or solids from gases, are microfiltration membranes. Gas membranes generally work because individual gases differ in their solubility and diffusivity through nonporous polymers. A few membranes operate by sieving, Knudsen flow, or chemical complexation.

Selective gas permeation has been known for generations, and the early use of palladium silver-alloy membranes achieved sporadic industrial use. Gas separation on a massive scale was used to separate U^{235} from U^{238} using porous (Knudsen flow) membranes. An upgrade of the membranes at Oak Ridge cost $1.5 billion. Polymeric membranes became economically viable about 1980, introducing the modern era of gas-separation membranes. H_2 recovery was the first major application, followed quickly by acid gas separation (CO_2/CH_4) and the production of N_2 from air.

Three basic mechanisms can be used for membranes in gas separation. They are types (*b*), (*c*), and (*d*) in Fig. 22-47. Membranes of type (*d*) are by far the dominant type.

The more permeable component is called the *fast gas,* so it is the one enriched in the permeate stream. Permeability through polymers is the product of solubility and diffusivity. The diffusivity of a gas in a membrane is inversely proportional to its kinetic diameter, a value determined from zeolite cage exclusion data (see Table 22-23 after Breck, *Zeolite Molecular Sieves,* Wiley, NY, 1974, p. 636).

Leading Examples These applications are commercial, some on a very large scale. They illustrate the range of application for gas-separation membranes. Unless otherwise specified, all use polymeric membranes.

Hydrogen Hydrogen recovery was the first large commercial membrane gas separation. Polysulfone fiber membranes became available in 1980 at a time when H_2 needs were rising, and these novel membranes quickly came to dominate the market. Applications include recovery of H_2 from ammonia purge gas, and extraction of H_2 from petroleum cracking streams. Hydrogen once diverted to low-quality fuel use is now recovered to become ammonia, or is used to desulfurize fuel, etc. H_2 is the fast gas.

Carbon Dioxide-Methane Much of the natural gas produced in the world is coproduced with an acid gas, most commonly CO_2 and/or H_2S. While there are many successful processes for separating the gases, membrane separation is a commercially successful competitor, especially for small installations. The economics work best for feeds with very high or very low CH_4 content. Methane is a slow gas; CO_2, H_2S, and H_2O are fast gases.

Oxygen-Nitrogen Because of higher solubility, in many polymers, O_2 is faster than N_2 by a factor of 5. Water is much faster still. Since simple industrial single-stage air compressors provide sufficient pressure to drive an air-separating membrane, moderate purity N_2 (95–99.5%) may be produced in low to moderate quantities quite economically by membrane separation. (Argon is counted as part of the nitrogen.) An O_2-enriched stream is a coproduct, but it is rarely of economic value. The membrane process to produce O_2 as a primary product has a limited market.

Helium Helium is a very fast gas, and may be recovered from natural gas through the use of membranes. More commonly, membranes are used to recover He after it has been used and become diluted.

Gas Dehydration Water is extremely permeable in polymer membranes. Dehydration of air and other gases is a growing membrane application.

Vapor Recovery Organic vapors are recovered from gas streams using highly permeable rubbery polymer membranes which are generally unsuitable for permanent gas separations because of poor selectivity. The high sorption of vapors in these materials makes them ideal for stripping and recovering vapors from gases.

Competing Processes Membranes are not the only way to make these separations, neither are they generally the dominant way. In many applications, membranes compete with cryogenic distillation and with pressure-swing adsorption; in others, physical absorption is the dominant method. The growth rate for membrane capacity is higher than that for any competitor.

Basic Principles of Operation Gas-separation literature often

TABLE 22-23 Kinetic Diameters for Important Gases

Penetrant	He	H_2	NO	CO_2	Ar	O_2	N_2	CO	CH_4	C_2H_4	Xe	C_3H_8
Kinetic dia, nm	0.26	0.289	0.317	0.33	0.34	0.346	0.364	0.376	0.38	0.39	0.396	0.43

TABLE 22-24 Gas-Permeation Units

Quantity	Engineering units	Literature units	SI units
Permeation rate	Standard cubic feet/minute		kmol/s
Permeation flux	ft^3/ft^2·day	cm/sec (STP)	kmol/m^2·s
Permeability	ft^3·ft/ft^2·day·psi	Barrers	kmol/m·s·Pa
Permeance	ft^3/ft^2·day·psi	Barrers/cm	kmol/m^2·s·Pa

TABLE 22-25 Barrer Conversion Factors

Quantity	Multiply	By	To get
Permeability	Barrers	3.348×10^{-19}	kmol/m·s·Pa
Permeability	Barrers	4.810×10^{-8}	ft^3(STP)/ft·psi·day
Permeance	Barrers/cm	3.348×10^{-17}	kmol/m^2·s·Pa
Permeance	Barrers/cm	1.466×10^{-6}	ft^3(STP)/ft^2·psi·day

TABLE 22-26 Industry-Specific Gas Measures

Industry-unit	How measured	Cubic feet per pound mole	kmol per mscf
STP, Mscf	1000 ft^3 at 32°F	359.3	1.262
Gas industry, Mscf	1000 ft^3 at 60°F	379.8	1.194
Air industry, Mnsf	1000 ft^3 at 70°F	387.1	1.172

uses nomenclature derived from distillation, a practice that will generally be followed here. L is the molar feed rate, V is the molar permeate rate, R is the molar residue ($L - V$). Mole fractions of components i, j, in the feed-residue phase will be x_i, x_j . . . and in the permeate phase y_i, y_j. . . . Stage cut, Θ, is permeate volume/feed volume, or V/L.

Basic Equations In "Background and Definitions," the basic equation for gas permeation was derived with the major assumptions noted. Equation (22-62) may be restated as:

$$J_i \sim N_i = (\rho_i/z)(p_{i,\text{feed}} - p_{i,\text{permeate}}) \tag{22-97}$$

where ρ_i is the permeability of component i through the membrane, J_i is the flux of component i through the membrane for the *partial pressure difference* (Δp) of component i. z is the effective thickness of the membrane. By choosing units appropriately, $J = \rho\Delta p$.

A similar equation may be written for a second component, j, and any additional number of components, employing partial pressures:

$$J_j = (\rho_j/z)(p_{j,\text{feed}} - p_{j,\text{permeate}}) \tag{22-98}$$

The total pressure is the sum of the partial pressures:

$$P_{\text{feed}} = \sum (p_{\text{feed}})_{i,j,\ldots} \tag{22-99}$$

$$P_{\text{permeate}} = \sum (p_{\text{permeate}})_{i,j\ldots} \tag{22-100}$$

For simplicity, consider a two component system. The volume fraction of a component is

$$x_i = \frac{p_{\text{feed}}}{P_{\text{feed}}} \tag{22-101}$$

$$y_i = \frac{p_{\text{permeate}}}{P_{\text{permeate}}} \tag{22-102}$$

When two species are permeating through a membrane, the ratio of their fluxes can be written following Eqs. (22-97) and (22-98) as:

$$\frac{J_i}{J_j} = \frac{\frac{\rho_i}{z}(p_{i,\text{feed}} - p_{i,\text{permeate}})}{\frac{\rho_i}{z}(p_{j,\text{feed}} - p_{j,\text{permeate}})} \tag{22-103}$$

Recalling Eq. (22-63), and restating it in the nomenclature for gas membranes:

$$\alpha = \frac{y_i/y_j}{x_i/x_j} \tag{22-104}$$

Defining the pressure ratio $\Phi = P_{\text{feed}}/P_{\text{permeate}}$ and applying Eqs. (22-99) through (22-102) gives:

$$\frac{J_i}{J_j} = \alpha\left[\frac{x_i - (y_i/\Phi)}{x_j - (y_j/\Phi)}\right] \tag{22-105}$$

Combining these equations and rearranging, the permeate composition may be solved explicitly:

$$y_i = \left(\frac{\Phi}{2}\right)\left[x_i + \frac{1}{\Phi} + \frac{1}{\alpha - 1} - \sqrt{\left(x_i + \frac{1}{\Phi} + \frac{1}{\alpha - 1}\right)^2 - \frac{4\alpha x_i}{(\alpha - 1)\Phi}}\right] \tag{22-106}$$

Equation (22-106) gives a permeate concentration as a function of the feed concentration at a stage cut, $\Theta = 0$, To calculate permeate composition as a function of Θ, the equation may be used iteratively if the permeate is unmixed, such as would apply in a test cell. The calculation for real devices must take into account the fact that the driving force is variable due to changes on both sides of the membrane, as partial pressure is a point function, nowhere constant. Using the same caveat, permeation rates may be calculated component by component using Eq. (22-98) and permeance values. For any real device, both concentration and permeation require iterative calculations dependent on module geometry.

Driving Force Gas moves across a membrane in response to a difference in chemical potential. Partial pressure is sufficiently proportional to be used as the variable for design calculations for most gases of interest, but fugacity must be used for CO_2 and usually for H_2 at high pressure. Gas composition changes as a gas passes along a membrane. As the fast gas passes through the membrane, x_i drops. Total pressure on the upstream side of the membrane drops because of frictional losses in the device. Frictional losses on the permeate side will affect the permeate pressure. The partial pressure of a component in the permeate may thus rise rapidly. Permeation rate is a point function, dependent on the difference in partial pressures at a point on the membrane. Many variables affect point partial pressures, among them are membrane structure, module design, and permeate gas-sweep rates. Juxtaposition of feed and permeate is a function of permeator design, and a rapid decline in driving force may result when it is not expected (see "Membrane System Design Features"). An additional complication may arise in a few cases from the Joule-Thompson effect during expansion of a gas through a membrane changing the temperature. High-pressure CO_2 is an example.

Plasticization Gas solubility in the membrane is one of the factors governing its permeation, but the other factor, diffusivity, is not always independent of solubility. If the solubility of a gas in a polymer is too high, plasticization and swelling result, and the critical structure that controls diffusion selectivity is disrupted. These effects are particularly troublesome with condensable gases, and are most often noticed when the partial pressure of CO_2 or H_2S is high. H_2 and He do not show this effect This problem is well known, but its manifestation is not always immediate.

Limiting Cases Equation (22-106) has two limiting cases for a binary system. First, when $\alpha \gg \phi$. In this case, selectivity is no longer very important.

$$y_i \cong x_i \frac{P_{\text{feed}}}{P_{\text{permeate}}} = x_i\Phi \tag{22-107}$$

Module design is very important for this case, as the high α may result in high permeate partial pressure. An example is the separation of H_2O from air.

Conversely, when $\Phi \gg \alpha$, pressure ratio loses its importance, and permeate composition is:

$$y_i \cong \frac{x_i\alpha}{[1 + x_i(\alpha - 1)]} \tag{22-108}$$

Module design for this case is of lesser importance.

Selectivity and Permeability

State of the Art A desirable gas membrane has high separating power (α) and high permeability to the fast gas, in addition to critical requirements discussed below. The search for an ideal membrane produced copious data on many polymers, neatly summarized by Robeson [*J. Membrane Sci.,* **62,** 165 (1991)]. Plotting log permeability versus log selectivity (α), an "upper bound" is found (see Fig. 22-73) which all the many hundreds of data points fit. The data were taken between 20–50°C, generally at 25 or 35°C.

The lower line in Fig. 22-73 shows the upper bound in 1980. Although no breakthrough polymers have been reported in the past few years, it would be surprising if these lines remain the state of the art forever.

The upper-bound line connects discontinuous points, but polymers exist near the bound for separations of interest. Whether these will be available as membranes is a different matter. A useful membrane requires a polymer which can be fabricated into a device having an active layer around 50 nm thick. At this thickness, membrane properties may vary significantly from bulk properties, although not by a factor of 2.

The data reported are *permeabilities,* not *fluxes.* Flux is propor-

TABLE 22-27 High-Performance Polymers for O_2/N_2*

Polymer	α (O_2/N_2)	ρ (O_2)—Barrers
Poly (trimethylsilylpropyne)	2.0	4000
Tetrabromo Bis A polycarbonate	7.47	1.36
Poly (tert-butyl acetylene)	3.0	300
Vectra polyester	15.3	0.00046
Poly (triazole)	9.0	1.2
Polypyrrolone	6.5	7.9

*Polymers that are near the upper bound and their characteristics.

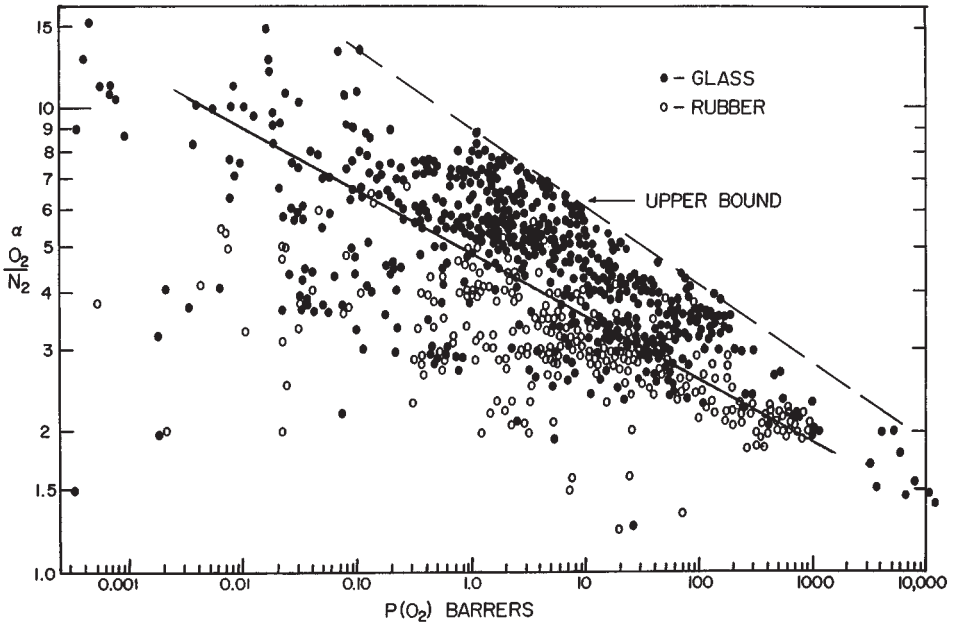


FIG. 22-73 Plot of separation factor versus permeability for many polymers, O_2/N_2. Abscissa—"Fast Gas Permeability, $\rho(O_2)$ Barrers." Ordinate—"Selectivity, α (O_2/N_2)."

tional to permeability/thickness. The separations designer must deal with real membranes, for which thickness is determined by factors outside the designer's control. It is vital that flux data are used in design.

Glassy polymers are significantly overrepresented in the high-selectivity region near the upper bound, and rubbery polymers are overrepresented at the high-permeability end, although the highest-permeability polymer discovered, poly(trimethylsilylpropyne) is glassy. Most of the polymers with interesting properties are noncrystalline. Current membrane-materials research is strongly focused on glassy materials and on attempts to improve diffusivity, as it seems more promising than attempts to increase solubility [Koros, *North Am. Membrane Soc. Sixth Annual Meeting*, Breckenridge, CO (1994)].

Robeson [*J. Membrane Sci.*, **62,** 165 (1991); *Polymer,* **35,** 4970 (1994)] has determined upper-bound lines for many permeant pairs in hundreds of polymers. These lines may be drawn from Eq. (22-109) and the data included in Table 22-28. These values will give ρ_i in Barrers; α is dimensionless. Robeson [op.cit., (1991); op. cit., (1994)] lists high-performance polymers for most of these gas pairs, like Table 22-28.

$$\log \rho_i = \log k - m \log \alpha_{ij} \qquad (22\text{-}109)$$

Temperature Effects A temperature increase in a polymer membrane permits larger segmental motions in the polymer, producing a dramatic increase in diffusivity. Countering this is a decrease in solubility. It increases the size of the gaps in the polymer matrix, decreasing diffusivity selectivity. The net result is that for a glassy polymer, permeability rises while selectivity declines. For organic permeants in rubbery polymers, this trend is often reversed.

TABLE 22-28 Upper-Bound Coordinates for Gas Pairs

Gas pair	log k	m
He/N_2	4.0969	1.0242
H_2/N_2	4.7236	1.5275
He/CH_4	3.6991	0.7857
H_2/CH_4	4.2672	1.2112
O_2/N_2	5.5902	5.800
He/O_2	3.6628	1.295
H_2/O_2	4.5534	2.277
CO_2/CH_4	6.0309	2.6264
He/H_2	2.9823	4.9535
He/CO_2	2.8482	1.220
H_2/CO_2	3.0792	1.9363

Plasticization and Other Time Effects Most data from the literature, including those presented above are taken from experiments where one gas at a time is tested, with α calculated as a ratio of the two permeabilities. If either gas permeates because of a high-sorption coefficient rather than a high diffusivity, there may be an increase in the permeability of all gases in contact with the membrane. Thus, the α actually found in a real separation may be much lower than that calculated by the simple ratio of permeabilities. The data in the literature do not reliably include the plasticization effect. If present, it results in the sometimes slow relaxation of polymer structure giving a rise in permeability and a dramatic decline in selectivity.

Other Caveats Transport in glassy polymers is different from transport in rubbery ones. In glassy polymers, there are two sites in which sorption may occur, and the literature dealing with dual-mode sorption is voluminous. The simplest case describes behavior when the downstream pressure is zero. It is of great help in understanding the theory but of limited value in practice. There are concerns about permeation of mixtures in glassy polymers with reports of crowding out and competitive sorption. Practical devices are built and operated for many streams, and the complications are often minor. But taking data independently determined for two pure gases and dividing them to obtain α in the absence of other facts is risky.

Gas-Separation Membranes

Organic Organic polymer membranes are the basis for almost all commercial gas-separation activity. Early membranes were cellulose esters and polysulfone. These membranes have a large installed base. New installations are dominated by specialty polymers designed for the purpose, including some polyimides and halogenated polycarbonates. In addition to skinned membranes, composites are made from "designer" polymers, requiring as little as 2 g/1000 m^2. The rapid rise of N_2/O_2 membranes in particular is the result of stunning improvements in product uniformity and quality. A few broken fibers in a

100 m^2 module results in the module's being scrapped.

Caulked Membrane manufacturing defects are unavoidable, and pinholes are particularly deleterious in gas-separation membranes. A very effective remedy is to **caulk** the membrane by applying a highly permeable, very thin topcoat over the finished membrane. While the coating will have poor selectivity, it will plug up the gross leaks while impairing the fast gas permeance only slightly. Unless the as-cast membrane is almost perfect, caulking dramatically improves membrane performance.

Metallic Palladium films pass H_2 readily, especially above 300°C. α for this separation is extremely high, and H_2 produced by purification through certain Pd alloy membranes is uniquely pure. Pd alloys are used to overcome the crystalline instability of pure Pd during heating-cooling cycles. Economics limit this membrane to high-purity applications.

Advanced Materials Experimental membranes have shown remarkable separations between gas pairs such as O_2/N_2 whose kinetic diameters (see Table 22-23) are quite close. Most prominent is the carbon molecular sieve membrane, which operates by ultramicroporous molecular sieving (see Fig. 22-48*c*). Preparation of large-scale permeators based on ultramicroporous membranes has proven to be a major challenge.

Catalytic A catalytic-membrane reactor is a combination heterogeneous catalyst and permselective membrane that promotes a reaction, allowing one component to permeate. Many of the reactions studied involve H_2. Membranes are metal (Pd, Ag), nonporous metal oxides, and porous structures of ceramic and glass. Falconer, Noble, and Sperry [in Noble and Stern (eds.), op. cit., pp. 669–709] review status and potential developments.

Membrane System Design Features For the rate process of permeation to occur, there must be a driving force. For gas separations, that force is partial pressure (or fugacity). Since the ratio of the component fluxes determines the separation, the partial pressure of each component at each point is important. There are three ways of driving the process: Either high partial pressure on the feed side (achieved by high total pressure), or low partial pressure on the permeate side, which may be achieved either by vacuum or by introduction of a sweep gas. Both of the permeate options have negative economic implications, and they are less commonly used.

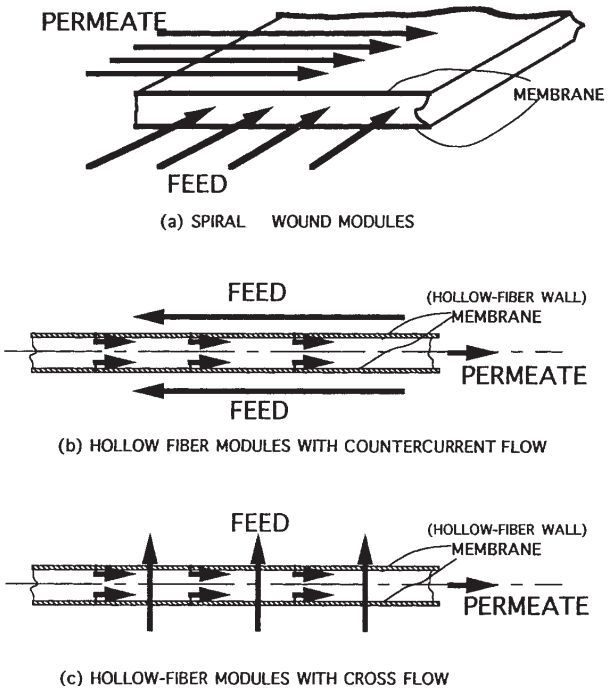


FIG. 22-74 Flow paths in gas permeators. (*Courtesy Elsevier.*)

Figure 22-74 shows three of the principal operating modes for gas membranes. A critical issue is the actual partial pressure of permeant at a point on the membrane. Flow arrangements for the permeate are very important in determining the efficiency of the separation, in rough analogy to the importance of arrangements in heat exchangers.

Spiral membranes are the usual way to form flat sheet into modules. They have the characteristic that the feed and the permeate move at right angles. Since the membrane is always cast on a porous support, point-permeate values are influenced by the substrate.

Hollow-fiber membranes may be run with shell-side or tube-side feed, cocurrent, countercurrent or in the case of shell-side feed and two end permeate collection, co- and countercurrent. Not shown is the scheme for feed inside the fiber, common practice in lower-pressure separations such as air.

The design of the membrane device will influence whether the membrane is operating near its theoretical limit. Sengupta and Sirkar [in Noble and Stern (eds.), op. cit., pp. 499-552] treat module design thoroughly (including numerical examples for most module configurations) and provide an extensive bibliography.

For a hollow-fiber device running with shell-side feed with the membrane on the outside, Giglia et al. [*Ind. Eng. Chem Research,* **29,** 1239–1248 (1991)] analyzed the effect of membrane-backing porosity on separation efficiency. The application is production of N_2 from air, the desired result being the lowest possible O_2 content in the retentate at a given stage cut. The modules used were operated cocurrent and countercurrent. If the porous-membrane backing prevented the permeate from mixing with the gas adjacent to the membrane, a result approximating cross-flow is expected. For the particular membrane structure used, the experimental result for cocurrent flow was quite close to the calculated cocurrent value, while for countercurrent flow, the experimental data were between the values calculated for the crosscurrent model and the countercurrent model. For a membrane to be commercially useful in this application, the mass transfer on the permeate side must exceed the crosscurrent model.

Air is commonly run with tube-side feed. The permeate is run countercurrent with the separating skin in contact with the permeate. (The feed gas is in contact with the macroporous back side of the membrane.) This configuration has proven to be superior, since the permeate-side mass-transfer problem is reduced to a minimum, and the feed-side mass-transfer problem is not limiting.

Partial Pressure Pinch An example of the limitations of the partial pressure pinch is the dehumidification of air by membrane. While O_2 is the fast gas in air separation, in this application H_2O is faster still. Special dehydration membranes exhibit α = 20,000. As gas passes down the membrane, the partial pressure of H_2O drops rapidly in the feed. Since the H_2O in the permeate is diluted only by the O_2 and N_2 permeating simultaneously, p_{H2O} rises rapidly in the permeate. Soon there is no driving force. The commercial solution is to take some of the dry air product and introduce it into the permeate side as a countercurrent sweep gas, to dilute the permeate and lower the H_2O partial pressure. It is in effect the introduction of a leak into the membrane, but it is a controlled leak and it is introduced at the optimum position.

Fouling Industrial streams may contain condensable or reactive components which may coat, solvate, fill the free volume, or react with the membrane. Gases compressed by an oil-lubricated compressor may contain oil, or may be at the water dew point. Materials that will coat or harm the membrane must be removed before the gas is treated. Most membranes require removal of compressor oil. The extremely permeable poly(trimethylsilylpropyne) may not become a practical membrane because it loses its permeability rapidly. Part of the problem is pore collapse, but it seems extremely sensitive to contamination even by diffusion pump oil and gaskets [Robeson, op. cit., (1994)].

A foulinglike problem may occur when condensable vapors are left in the residue. Condensation may result which in the best case results in blinding of the membrane, and in the usual case, destruction of the membrane module. Dew-point considerations must be part of any gas-membrane design exercise.

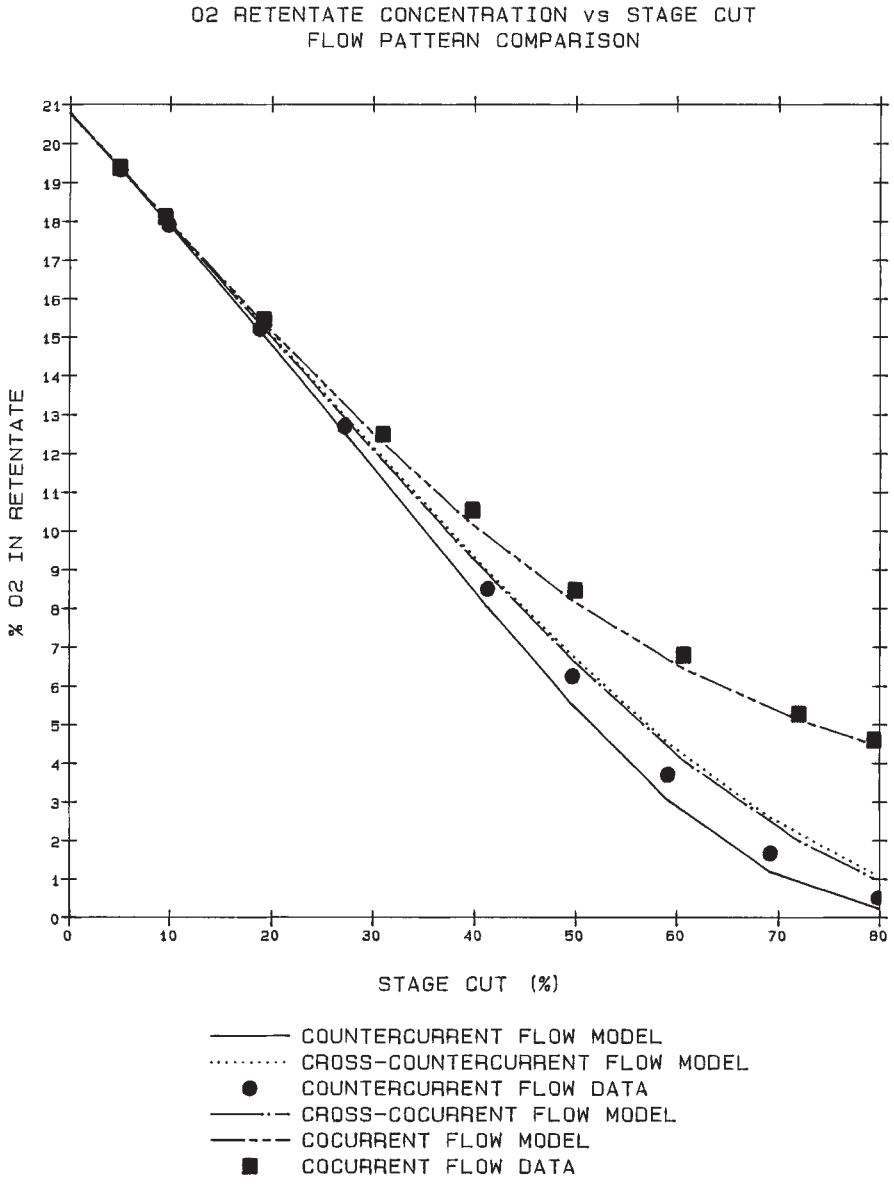


FIG. 22-75 Air fractionation by membrane. O_2 in retentate as a function of feed fraction passed through the membrane (stage cut) showing the different result with changing process paths. Process has shell-side feed at 690 kPa (abs) and 298 K. Module comprised of hollow fibers, diameter 370 μm od × 145 μm id × 1500 mm long. Membrane properties $\alpha = 5.7$ (O_2/N_2), permeance for $O_2 = 3.75 \times 10^{-6}$ Barrer/cm. (*Courtesy Innovative Membrane Systems/ Praxair.*)

Modules and Housings Modern gas membranes are packaged either as hollow-fiber bundles or as spiral-wound modules. The former uses extruded hollow fibers. Tube-side feed is preferable, but it is limited to about 1.5 MPa. Higher-pressure applications are usually fed on the shell side. A large industrial permeator contains fibers 400 μm by 200 μm i.d. in a 6-inch shell ten feet long. Flat-sheet membrane is wound into spirals, with an 8- by 36-inch permeator containing 25 m^2 of membrane. Both types of module are similar to those illustrated in "Background and Definitions." Spiral modules are useful when feed flows are very high and especially in vapor-permeation applications. Otherwise, fiber modules have a large and growing share of the market.

Energy Requirements The thermodynamic minimum energy requirement to separate a metric ton of N_2 from air and compress it to atmospheric pressure at 25°C is independent of separation method, 20.8 MJ or 5.8 kWh. In practice, a cryogenic distillation plant requires twice this energy, and it produces a very pure product as a matter of course. The membrane process requires somewhat more energy than distillation at low purity and much more energy at high purity. Membranes for O_2-reduced air are economical and are a rapidly growing application, but not because of energy efficiency. Figure 22-75 may be used to estimate membrane energy requirements. From the required purity, locate the stage cut on either of the countercurrent flow curves. The compressor work required is calculated using the pressure and the term (product flow rate)/$(1 - \Theta)$. The N_2-rich product is produced at pressure, and the O_2-enriched permeate is vented. For

example, if gas is required containing 97 percent inerts, assume the product composition would be 96 percent N_2, 2 percent O_2, 1 percent Ar and 3 percent O_2, giving a calculated molar mass of 28.2. One tonne would thus contain 35.4 kmol. For 98 percent inerts, Fig. 22-75 shows a stage cut of 67 percent when operating at 690 kPa (abs) and 25°C. Therefore, 35.5/(1 − 0.67) = 108 kmol of air are required as feed. The adiabatic compression of 108 kmol of air from atmospheric pressure and 300K (it would subsequently be cooled to 273 + 25 = 298K) requires 192 kWh. Assuming 75 percent overall compressor + driver efficiency, 256 kWh are required. For comparison, a very efficient, large N_2 distillation plant would produce 99.99 percent N_2 at 690 kPa for 113 kWh/metric ton. The thermodynamic minimum to separate (N_2 + Ar) and deliver it at the given P and T is 72 kWh.

Economics It is ironic that a great virtue of membranes, their versatility, makes economic optimization of a membrane process very difficult. Designs can be tailored to very specific applications, but each design requires a sophisticated computer program to optimize its costs. Spillman [in Noble and Stern (eds)., op. cit., pp. 589–667] provides an overall review and numerous specific examples including circa 1989 economics.

Rules of Thumb With a few notable exceptions such as H_2 through Pd membranes, membrane separations are not favored when a component is required at high purity. Often, membranes serve these needs by providing a moderate purity product which may be inexpensively upgraded by a subsequent process. Increasing the purity of N_2 by the introduction of H_2 or CH_4 to react with unwanted O_2 is a good example. Unless permeates are recycled, high product purity is accompanied by lower product recovery.

Pressure ratio (Φ) is quite important, but transmembrane ΔP matters as well. Consider the case of a vacuum permeate ($\Phi = \infty$): The membrane area will be an inverse function of P. Φ influences separation and area, transmembrane ΔP influences area.

In a binary separation, the highest purity of integrated permeate occurs at $\Theta = 0$. Purity decreases monotonically until it reaches the feed purity at $\Theta = 1$. In a ternary system, the residue concentration of the gas with the intermediate permeability will reach a maximum at some intermediate stage cut.

Concentration polarization is a significant problem only in vapor separation. There, because the partial pressure of the penetrant is normally low and its solubility in the membrane is high, there can be depletion in the gas phase at the membrane. In other applications it is usually safe to assume bulk gas concentration right up to the membrane.

Another factor to remember is that for $\alpha = 1$, or for $\Phi = 1$, or for $(1/\Theta) = 1$ there is no separation at all. Increasing any of the quantities as defined make for a better separation, but the improvement is diminishing in all cases as the value moves higher. An example of the economic tradeoff between permeability and α is illustrated in Fig. 22-76 where the economics are clearly improved by sacrificing selectivity for flux.

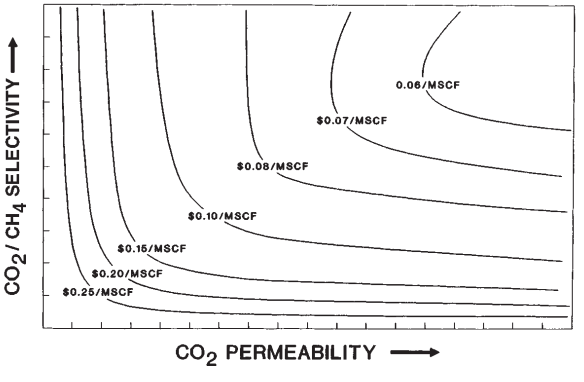


FIG. 22-76 Constant-cost lines as a function of permeability and selectivity for CO_2/CH_4. Cellulose-acetate membrane "mscf" is one thousand standard cubic feet. (*Courtesy W. R. Grace.*)

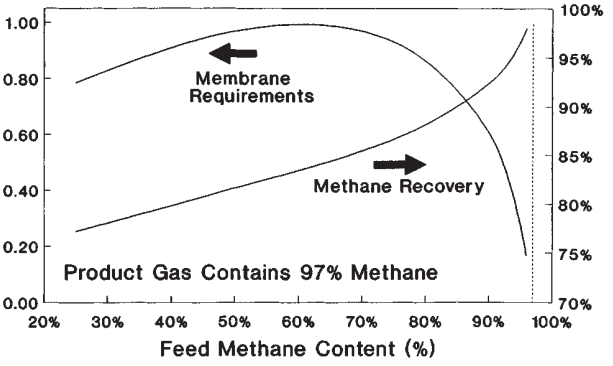


FIG. 22-77 Influence of feed purity on total membrane area when the residue gas at fixed purity is the product. Feed-gas volume is constant. CO_2/CH_4 cellulose-acetate membrane, $\alpha = 21$. (*Courtesy W. R. Grace.*)

Compression If compression of either feed or permeate is required, it is highly likely that compression capital and operating costs will dominate the economics of the gas-separation process. In some applications, pressure is essentially "free," such as when removing small quantities of CO_2 from natural gas. The gas is often produced at pressure, but is compressed for transmission anyway, and since the residue constitutes the product, it continues downstream at pressure. H_2 frequently enters the separation process at pressure, an advantage for membranes. Unlike CH_4, the H_2 is in the permeate, and recompression may be a significant cost. A relative area cure for CO_2/CH_4 is shown in Fig. 22-77. When the permeate is the product (H_2, CO_2) the increasing membrane area shown in Fig. 22-78 is largely the effect of more gas to pass through the membrane, since the curve is based on a constant volume of feed gas, not a constant output of H_2. The facts of life in compressor economics are in painful opposition to the desires of the membrane designer. Pressure ratios higher than six become expensive; vacuum is very expensive, and scale is important. Because of compressor economics, staging membranes with recompression is unusual. Designers can assume that a flow sheet that mixes unlike streams or reduces pressure through a throttling valve will increase cost in most cases.

Product Losses Account must be taken of the product loss, the slow gas in the permeate (such as CH_4), or the fast gas in the residue (such as H_2). Figure 22-79 illustrates the issue for a membrane used to purify natural gas from 93 percent to pipeline quality, 98 percent. In the upper figure, the gas is run through a permeator bank operating as a single stage. For the membrane and module chosen, the permeate contains 63 percent CH_4. By dividing the same membrane area into

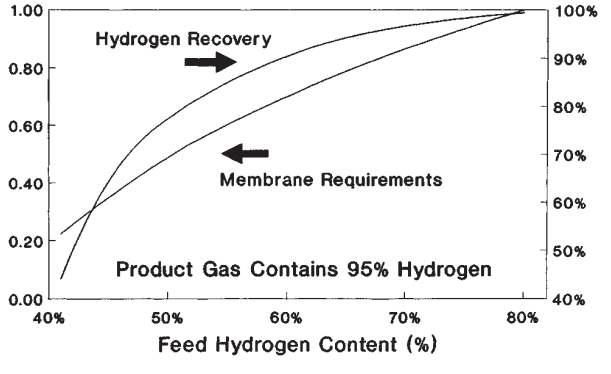
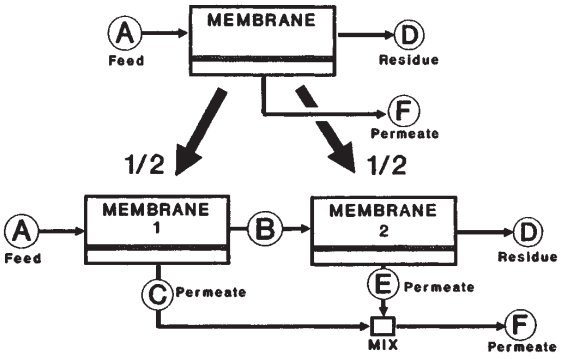


FIG. 22-78 Influence of feed purity on total membrane area when the permeate gas at fixed purity is the product. Feed-gas volume is constant. H_2/CH_4 cellulose-acetate membrane, $\alpha = 45$. (*Courtesy W. R. Grace.*)



		A	B	C	D	E	F
CO2	%	7.0	3.6	43.9	2.0	27.3	36.6
CH4	%	93.0	96.2	56.1	98.0	72.7	63.4
RATE	Ratio	1.00	0.92	0.08	0.86	0.06	0.14
PRESS	psia	860	860	15	860	15	15

FIG. 22-79 Effect on permeate of dividing a one-stage separation into two equal stages having the same total membrane area. Compositions of A, D, and F are equal for both cases. (*Courtesy W. R. Grace.*)

two stages, two permeates (or more) may be produced, one of which may have significantly higher economic value than the single mixed permeate. In fact, where CH_4 is involved, another design parameter is the local economic value of various waste streams as fuel.

Membrane Replacement Membrane replacement is a significant cost factor, but membrane life and reliability are now reasonable. Membranes are more susceptible to operating upsets than more traditional equipment, but their field-reliability record in properly engineered, properly maintained installations is good to excellent. In N_2 separations, membrane life is very long.

Competing Technologies The determination of which separation technique is best for a specific application is a dynamic function of advances in membranes and several other technologies. At this writing, very small quantities of pure components are best obtained by purchase of gas in cylinders. For N_2, membranes become competitive at moderate flow rates where purity required is <99.5 percent. At higher flow rates and higher purity, *pressure swing adsorption* (PSA) is better (see Sec. 16: "Adsorption and Ion Exchange"). At still higher volumes, delivered liquid N_2, pipeline N_2, or on-site distillation will be superior. For O_2, membranes have little economic importance. The problem is the economic cost of using vacuum on the permeate side, or the equally unattractive prospect of compressing the feed and operating at low stage cut. For H_2, membranes are dominant when the feed is at high pressure, except for high purity (excepting Pd noted above) and very large volume. Higher purity or lower feed pressure favor PSA. Very high volume favors cryogenic separation. For CH_4, membranes compete at low purity and near pipeline (98 percent) purity, but distillation and absorption are very competitive at large scale and for intermediate CO_2 contamination levels.

Membranes are found as adjuncts to most conventional processes, since their use can improve overall economics in cases where membrane strength coincides with conventional process weakness.

PERVAPORATION

Process Description **Pervaporation** is a separation process in which a liquid mixture contacts a nonporous permselective membrane. One component is transported through the membrane preferentially. It evaporates on the downstream side of the membrane leaving as a vapor. The name is a contraction of permeation and evaporation. Permeation is induced by lowering partial pressure of the permeating component, usually by vacuum or occasionally with a sweep gas. The permeate is then condensed or recovered. Thus, three steps are necessary: Sorption of the permeating components into the membrane, diffusive transport across the nonporous membrane, then desorption into the permeate space, with a heat effect. Pervaporation membranes are chosen for high selectivity, and the permeate is often highly purified.

In the flow schematic (Fig. 22-80), the condenser controls the vapor pressure of the permeating component. The vacuum pump, as shown, pumps both liquid and vapor phases from the condenser. Its major duty is the removal of noncondensibles. Early work in pervaporation focused on organic-organic separations. Many have been demonstrated; few if any have been commercialized. Still, there are prospects for some difficult organic separations.

An important characteristic of pervaporation that distinguishes it from distillation is that it is a rate process, not an equilibrium process. The more permeable component may be the less-volatile component. Pervaporation has its greatest utility in the resolution of azeotropes, as an adjunct to distillation. Selecting a membrane permeable to the minor component is important, since the membrane area required is roughly proportional to the mass of permeate. Thus pervaporation devices for the purification of the ethanol-water azeotrope (95 percent ethanol) are always based on a hydrophilic membrane.

Pervaporation membranes are of two general types. **Hydrophilic membranes** are used to remove water from organic solutions, often from azeotropes. **Hydrophobic membranes** are used to remove organic compounds from water. The important operating characteristics of hydrophobic and hydrophilic membranes differ. Hydrophobic membranes are usually used where the solvent concentration is about

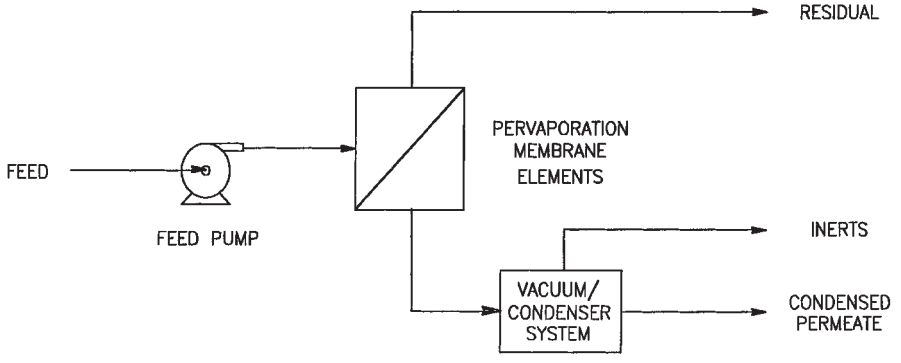


FIG. 22-80 Simplified flow schematic for a pervaporation system. Heated feed enters from left through a feed pump. Heaters in a recirculating feed loop may be required (not shown). Stripped liquid exits at the top of the pervaporation membrane. Vapor exits at the bottom to a condenser. Liquid and noncondensibles are removed under vacuum. (*Courtesy Hoechst Celanese.*)

6 percent or less—above this value, other separations methods are usually cheaper unless the flow rate is small. At low-solvent levels the usual membrane (silicone rubber) is not swollen appreciably, and movement of solvent into the membrane makes depletion of solvent in the boundary layer (concentration polarization) an important design problem. Hydrophilic pervaporation membranes operate such that the upstream portion is usually swollen with water, while the downstream face is low in water concentration because it is being depleted by vaporization. Fluxes are low enough (<5 kg/m²·hr) that boundary layer depletion (liquid side) is not limiting.

The simplifying assumptions that make Fick's law useful for other processes are not valid for pervaporation. The activity gradient across the membrane is far more important than the pressure gradient. Equation (22-110) is generally used to describe the pervaporation process:

$$J_i = -D_i C \frac{d \ln a_i}{dz} \qquad (22\text{-}110)$$

where a_i is the activity coefficient of component i.

This equation is not particularly useful in practice, since it is difficult to quantify the relationship between concentration and activity. The Flory-Huggins theory does not work well with the cross-linked semi-crystalline polymers that comprise an important class of pervaporation membranes. Neel (in Noble and Stern, op. cit., pp. 169–176) reviews modifications of the Stefan-Maxwell approach and other equations of state appropriate for the process.

A typical permeant-concentration profile in a pervaporation membrane is shown in Fig. 22-81. The concentration gradient at the permeate (vapor side) of the hydrophilic membrane is usually rate controlling. Therefore the downstream pressure (usually controlled by condenser temperature) is very important for flux and selectivity. Since selectivity is the ratio of fluxes of the components in the feed, as downstream pressure increases, membrane swelling at the permeate interface increases, and the concentration gradient at the permeate interface decreases. The permeate flux drops, and the more swollen membrane is less selective. A rise in permeate pressure may result in a drastic drop in membrane selectivity. This effect is diminished at low water concentrations, where membrane swelling is no longer dominant. In fact, when the water concentration drops far enough, permeate backpressure looses its significance. (See Fig. 22-82.)

For rubbery membranes (hydrophobic), the degree of swelling has less effect on selectivity. Thus the permeate pressure is less critical to the separation, but it is critical to the driving force, thus flux, since the vapor pressure of the organic will be high compared to that of water.

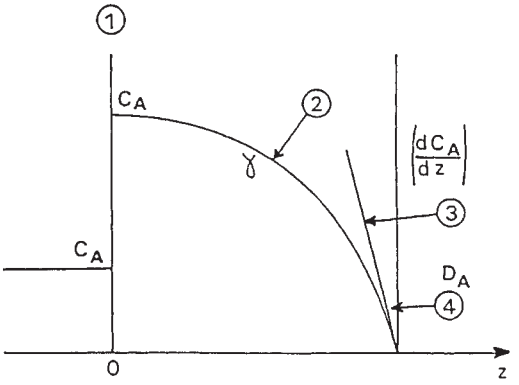


FIG. 22-81 Permeant-concentration profile in a pervaporation membrane. 1—Upstream side (swollen). 2—Convex curvature due to concentration-dependent permeant diffusivity. 3—Downstream concentration gradient. 4—Exit surface of membrane, depleted of permeant, thus unswollen. (*Courtesy Elsevier.*)

Definitions Following the practice presented under "Gas-Separation Membranes," distillation notation is used. Literature articles often use mass fraction instead of mole fraction, but the substitution of one to the other is easily made.

$$\beta \equiv \frac{y_i}{x_i} \qquad (22\text{-}111)$$

where β is the enrichment factor. β is related to α, [Equation (22-104)] the separation factor by

$$\beta = \frac{\alpha}{1 + (\alpha - 1)x_i} \qquad \alpha = \frac{\beta(1 - x_i)}{1 - x_i\beta} \qquad (22\text{-}112)$$

α is larger than β, and conveys more meaning when the membrane approaches the ideal. β is preferred in pervaporation because it is easier to use in formulations for cost, yield, and capacity. In fact, note that neither factor is constant, and that both generally change with x_i and temperature.

Operational Factors In industrial use, pervaporation is a continuous-flow single-stage process. Multistage cascade devices are unusual. Pervaporation is usually an adjunct separation, occasionally a principal one. It is used either to break an azeotrope or to concentrate a minor component. Large stand-alone uses may develop in areas

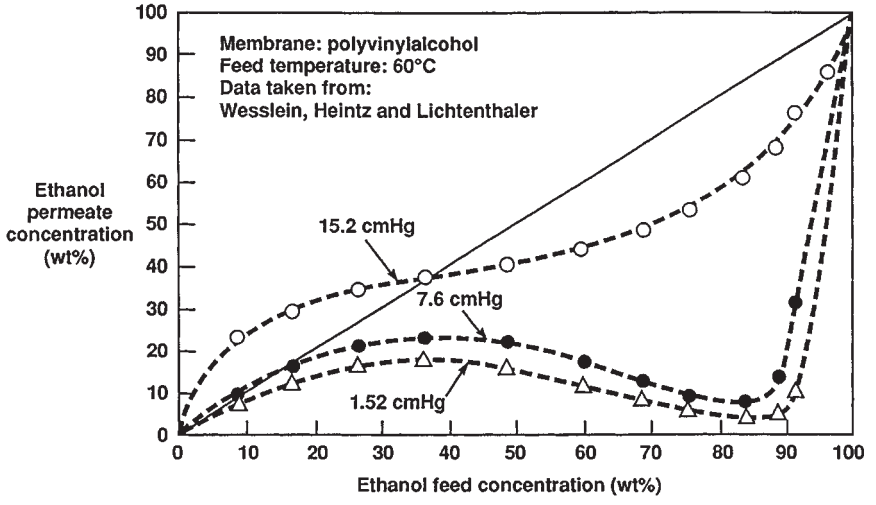


FIG. 22-82 Pervaporation schematic for ethanol-water. The illustration shows the complex behavior for a simple system at three pressures. Only the region above 90 percent is of commercial interest. (*Courtesy Elsevier.*)

where distillation is at a disadvantage, such as with closely boiling components, but these developments, have not yet been made. Notable exceptions occur when a stream is already fairly pure, such as a contaminated water source, or isopropanol from microelectronics fabrication washing containing perhaps 15 percent water.

In continuous flow, the feed will begin with concentration ($x_{i,\text{feed}}$) and be stripped until it reaches some desired ($x_{i,\text{residue}}$). If significant mass is removed from the feed, it will cool, since the general rule for liquids is that the latent heat exceeds the specific heat per °C by two orders of magnitude (more for water). So the membrane has a concentration gradient and a temperature gradient both across it and along it. Pervaporation is a complex multigradient process.

The term β is not constant for some important separations. Even worse, it can exhibit maxima that make analytic treatment difficult. Operating diagrams are often used for preliminary design rather than equations. Because of the very complex behavior in the membrane as concentrations change, all design begins with an experiment. For water removal applications, design equations often mispredict the rate constants as the water content of the feed approaches zero. The estimates tend to be lower than the experimental values, which would lead to overdesign. Therefore it is necessary to obtain experimental data over the entire range of water concentrations encountered in the separation. Once the kinetic data are available, heat transfer and heat capacity are the problem. It is general practice to pilot the separation on a prototype module to measure the changes due to thermal effects. This is particularly true for water as the permeant, given its high latent heat.

For removal of an organic component from water, swelling of the organophillic membrane would result in a higher flux and lower α. At organic levels below about 10 percent, that has not been a major problem. In most applications, boundary-layer mass-transfer limitations become limiting. Pilot data must therefore be taken with hydrodynamic similarity to the module that will be used and the actual organic permeation rate may become limited by the boundary layer. In organic-organic pervaporation, membrane swelling is a major concern.

Vapor Feed A variant on pervaporation is to use vapor, rather than liquid, as a feed. While the resulting process could be classified along with gas-separation membranes, it is customarily regarded as pervaporation.

The residue at the top of a distillation column is a vapor, so there is logic in using it as the feed to a membrane separator. Weighed against the obvious advantage are disadvantages of vapor handling (compressors cost more than pumps) and equipment size to handle the larger vapor volume. When the more volatile component permeates, heat must be added to maintain superheat. The vapor feed technique has been used in a few large installations where the advantages outweigh the disadvantages.

Leading Examples

Dehydration The growing use of isopropanol as a clean-rinse fluid in microelectronics produces significant quantities of an 85–90 percent isopropanol waste. Removing the water and trace contaminants is required before the alcohol can be reused. Pervaporation produces a 99.99 percent alcohol product in one step. It is subsequently polished to remove metals and organics. In Europe, dehydration of ethanol is the largest pervaporation application. For the very large ethanol plants typical of the United States, pervaporation is not competitive with thermally integrated distillation.

Organic from Water An area where pervaporation may become important is in flavors, fragrances, and essential oils. Here, high-value materials with unique properties are recovered from aqueous or alcohol solutions.

Pollution Control Pervaporation is used to reduce the organic loading of a waste stream, thus effecting product recovery and a reduction in waste-treatment costs. An illustration is a waste stream containing 11 percent (wt) *n*-propanol. The residue is stripped to 0.5 percent and 96 percent of the alcohol is recovered in the permeate as a 45 percent solution. This application uses a hydrophobic, rubbery membrane. The residue is sent to a conventional waste-treatment plant.

Pervaporation Membranes Pervaporation has a long history, and many materials have found use in pervaporation experiments. Cellulosic-based materials have given way to polyvinyl alcohol and blends of polyvinyl alcohol and acrylics in commercial water-removing membranes. These membranes are typically solution cast (from water) on ultrafiltration membrane substrates. It is important to have enough cross linking in the final polymer to avoid dissolution of the membrane in use. A very thin membrane with little penetration into the UF substrate is required. The substrate can be a problem, as it provides significant pressure drop to the vapor passing through it which, as mentioned above, has serious ramifications for flux and separation efficiency. Many new membranes are under development. Ion-exchange membranes, and polymers deposited by or polymerized by plasma, are frequently mentioned in the literature.

Modules Every module design used in other membrane operations has been tried in pervaporation. One unique requirement is for low hydraulic resistance on the permeate side, since permeate pressure is very low (0.1–1 Pa). The rule for near-vacuum operation is the bigger the channel, the better the transport. Another unique need is for heat input. The heat of evaporation comes from the liquid, and intermediate heating is usually necessary. Of course economy is always a factor. Plate-and-frame construction was the first to be used in large installations, and it continues to be quite important. Some smaller plants use spiral-wound modules, and some membranes can be made as capillary bundles. The capillary device with the feed on the inside of the tube has many advantages in principle, such as good vapor-side mass transfer and economical construction, but it is still limited by the availability of membrane in capillary form.

SELECTION OF BIOCHEMICAL SEPARATION PROCESSES

General References: Albertsson, *Partition of Cell Particles and Macromolecules,* 3d ed., John Wiley & Sons, New York, 1986. Belter, Cussler, and Hu, *Bioseparations,* Wiley Interscience, New York, 1988. Cooney and Humphrey (eds.), *Comprehensive Biotechnology,* vol. 2, Pergamon, Oxford, 1985. Janson and Ryden (eds.), *Protein Purification,* VCH, New York, 1989. Scopes, *Protein Purification,* 2d ed., Springer-Verlag, New York, 1987. Stephanopoulos (ed.), *Biotechnology,* 2d ed., vol. 3, VCH, Weinheim, 1993. Walter, Brooks, and Fisher (eds.), *Partitioning in Aqueous Two-Phase Systems,* Academic Press, Orlando, FL, 1985.

GENERAL BACKGROUND

The biochemical industry derives its products from two primary sources. Natural products are yielded by plants, animal tissue, and fluids, and obtained via fermentation from bacteria, molds and fungi, and from mammalian cells. Products can also be obtained by recombinant methods through the insertion of foreign DNA directly into the hosting microorganism to allow overproduction of the product in this unnatural environment. The range of bioproducts is enormous, and the media in which they are produced are generally complex and ill-defined, containing many unwanted materials in addition to the desired product. The product is invariably at low concentration. The goals of downstream processing operations include removal of these unwanted impurities, bulk-volume reduction with concomitant concentration of the desired product, and, for protein products, transfer of the protein to an environment where it will be stable and active, ready for its intended application. This requires on average three to six separate processing steps. Some of the purification methods in general use are shown in Fig. 22-83 [Bonnerjea et al., *Bio/Technology,* **4,** 954–958 (1986)] which indicates the average stage at which different methods are used in the downstream processing train. A general strategy for downstream processing of biological materials and the types of operations that may be used in the different steps is shown in Fig. 22-84 [see also Ho, in M. R. Ladisch et al. (eds.), *Protein Purification from Molecular Mechanisms to Large-Scale Processes,* ACS Symp. ser.

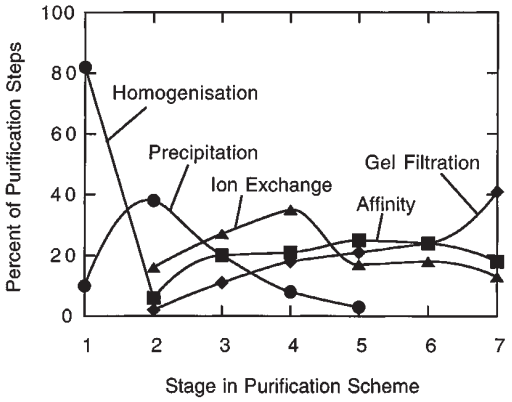


FIG. 22-83 Frequency of use of purification methods at different stages in purification schemes published in the literature. (*Adapted from Bonnerjea et al., op. cit.*)

427, ACS, Washington DC, 1990, pp. 14–34]. Section 24 in this handbook provides a general discussion of biochemical engineering.

Low-molecular-weight products, generally secondary metabolites such as alcohols, carboxylic and amino acids, antibiotics, and vitamins, can be recovered using many of the standard operations such as liquid-liquid extraction, adsorption and ion-exchange, described elsewhere in this handbook. Proteins require special attention, however, as they are sufficiently more complex, their function depending on the integrity of a delicate three-dimensional tertiary structure that can be disrupted if the protein is not handled correctly. For this reason, this section focuses primarily on protein separations. Cell separations, as a necessary part of the downstream processing sequence, are also covered.

Techniques used in bioseparations depend on the nature of the product (i.e., the unique properties and characteristics which provide a "handle" for the separation), and on its state (i.e., whether soluble or insoluble, intra- or extracellular, etc.). All early isolation and recovery steps remove whole cells, cellular debris, suspended solids, and colloidal particles, concentrate the product, and, in many cases, achieve some degree of purification, all the while maintaining high yield. For intracellular compounds, the initial harvesting of the cells is important

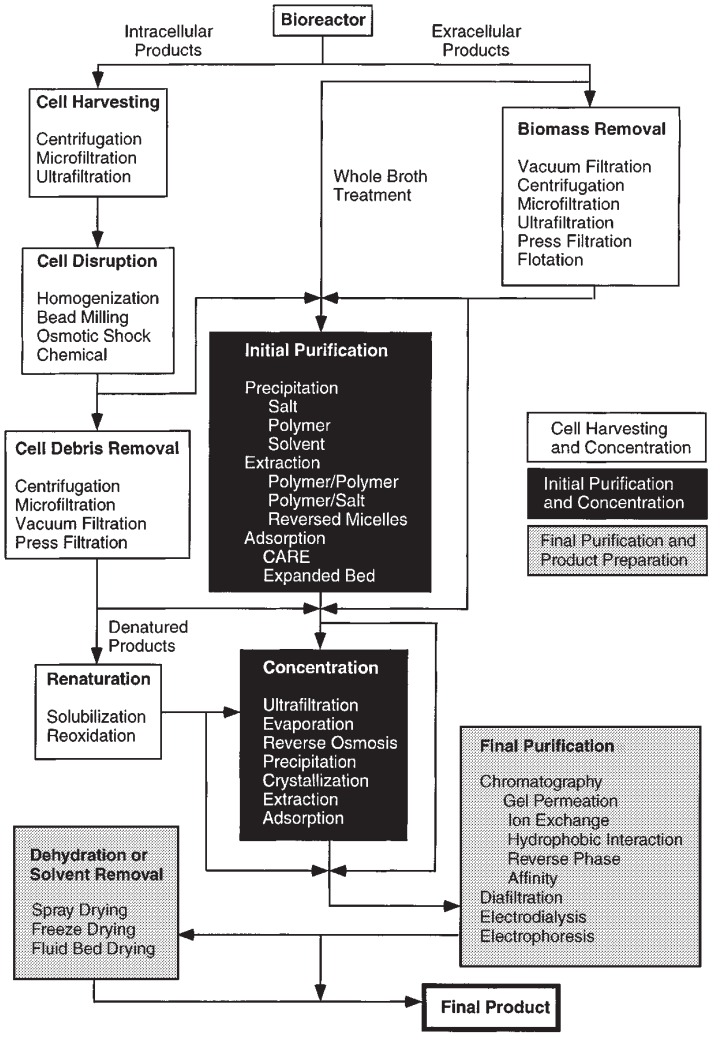


FIG. 22-84 General stages in downstream processing for protein production indicating representative types of operations used at each stage.

for their concentration prior to release of the product. Following this phase, a range of purification steps is employed to remove the remaining impurities and enhance the product purity; this purification phase, in turn, is followed by polishing steps to remove the last traces of contaminating components and process-related additions (e.g., buffer salts, detergents, etc.), and to prepare the product for storage and/or distribution. The prevention and/or avoidance of contamination is another important goal of downstream processing.

Even for good yields of 80 to 95 percent per step, the overall yield can be poor for any process that requires a large number of steps. Thus, careful consideration must be given to optimization of the process in terms of both the unit operations themselves, and their sequencing. It is usually desirable to reduce the process volume early in the downstream processing, and to remove any components that can be removed fairly easily (particulates, small solutes, large aggregates, nucleic acids, etc.) so as not to overly burden the more refined separation processes downstream. Possible shear and temperature damage, and deactivation by endogenous proteases must be considered in the selection of separation processes.

The purification of proteins to be used for therapeutic purposes presents more than just the technical problems associated with the separation process. Owing to the complex nature and intricate three-dimensional structure, the routine determination of protein structure as a quality-control tool, particularly in its final medium for use, is not well established. In addition, the complex nature of the human immune system allows for even minor quantities of impurities and contaminants to be biologically active. Thus, regulation of biologics production has resulted in the concept of the process defining the product since even small and inadvertent changes in the process may affect the safety and efficacy of the product. Indeed, it is generally acknowledged that even trace amounts of contaminants introduced from other processes, or contaminants resulting from improper equipment cleaning can compromise the product. From a regulatory perspective, then, operations should be chosen for more than just efficiency. The consistency of the unit operation, particularly in the face of potentially variable feed from the culture/fermentation process, is the cornerstone of the process definition. Operations that lack robustness or are subject to significant variation should not be considered. Another aspect of process definition is the ability to quantify the operation's performance. Finally, the ease with which the equipment can be cleaned in a verifiable manner should play a role in unit-operation selection.

In the development of new products, optimization of the fermentation medium for titer only often ignores the consequences of the medium properties on subsequent downstream processing steps such as filtration and chromatography. It is imperative, therefore, that there be effective communication and understanding between workers on the upstream and downstream phases of the product development if rational trade-offs are to be made to ensure overall optimality of the process. One example is to make the conscious decision, in collaboration with those responsible for the downstream operations, whether to produce a protein in an unfolded form or in its native folded form; the purification of the aggregated unfolded proteins is simpler than that of the native protein, but the refolding process itself to obtain the product in its final form may lack scalability.

INITIAL PRODUCT HARVEST AND CONCENTRATION

The initial processing steps are determined to a large extent by the location of the product species, and generally consist of cell/broth separation and/or cell-debris removal. For products retained within the biomass during production, it is first necessary to concentrate the cell suspension before homogenization or chemical treatment to release the product. Clarification to remove the suspended solids is the process goal at this stage.

Regardless of the location of the protein and its state, cell separation needs to be inexpensive, simple, and reliable, as large amounts of fermentation-broth dilute in the desired product may be handled. The objectives are to obtain a well-clarified supernatant and solids of maximum dryness, avoiding contamination by using a contained operation. Mechanical methods, almost exclusively centrifugation and cross-flow filtration, are preferred for cell separations [Datar and Rosen, in Stephanopoulos (ed.), op. cit., pp. 369–503].

Intracellular products can be present either as folded, soluble proteins, or as dense masses of unfolded protein (inclusion bodies). For these products, it is first necessary to concentrate the cell suspension before effecting release of the product. Filtration can result in a suspension of cells that can be of any desired concentration up to 15–17 percent, and that can be diafiltered into the desired buffer system. In contrast, the cell slurry that results from centrifugation will either be that of a dry mass (requiring resuspension but substantially free of residual broth, i.e., from a tubular bowl centrifuge) or a wet slurry (containing measurable residual broth and requiring additional resuspension). During the separation, conditions which result in cell lysis (such as extremes in temperature) must be avoided. In addition, while soluble protein is generally protected from shear and external proteolysis, these proteins are still subject to thermal denaturation.

For extracellular products, which are invariably water-soluble, the goal is the removal of whole cells (clarification) and, in the case of typical protein products, the removal of dissolved low-molecular-weight compounds. This must be done under relatively gentle conditions to avoid undesired denaturation of the product. Again, either filtration or centrifugation can be applied. Filtration results in a cell-free supernatant with dilution associated with the diafiltration of the final cell slurry. Centrifugation, regardless of the mode, will result in a small amount of cells in the centrate, but there is no dilution of the supernatant. During the process development careful studies should be conducted to examine the effects of pH and ionic strength on the yield, as cells and cell debris may retain the product through charge interactions. If the broth or cell morphology does not allow for filtration or if dry cell mass is required, tubular-bowl centrifugation is typically utilized. It should be noted that plant and animal cells cannot sustain the same degree of applied shear as microbial cells, and thus cross-flow filtration or classical centrifugation may not be applicable. Alternatives using low-shear equipment under gentle conditions are often employed in these situations.

For whole broths the range of densities and viscosities encountered affect the concentration factor that can be attained in the process, and can also render cross-flow filtration uneconomical because of the high pumping costs, and so on. Often, the separation characteristics of the broth can be improved by broth conditioning using physiocochemical or biological techniques, usually of a proprietary nature. The important characteristics of the broth are rheology and conditioning.

Centrifugation Centrifugation relies on the enhanced sedimentation of particles of density different from that of the surrounding medium when subjected to a centrifugal-force field [Axelsson, in Cooney and Humphrey (eds.), op. cit., pp. 325–346] (see also Sec. 18: "Liquid-Solid Operations and Equipment"). Advantages of centrifugal separations are that they can be carried out continuously and have short retention times, from a fraction of a second to seconds, which limit the exposure time of sensitive biologicals to shear stresses. Yields are high, provided that temperature and other process conditions are adequately controlled. They have small space requirements, and an adjustable separation efficiency makes them a versatile unit operation. They can be completely closed to avoid contamination, and, in contrast to filtration, no chemical external aids are required that can contaminate the final product. The ability now to contain the aerosols typically generated by centrifuges adds to their operability and safety.

Sedimentation rates must be sufficiently high to permit separation, and can be enhanced by modifying solution conditions to promote the aggregation of proteins or impurities. An increase in precipitation of the contaminating species can often be accomplished by a reduction in pH, or an elevation in temperature. Flocculating agents, which include polyelectrolytes, polyvalent cations, and inorganic salts, can cause a 2000-fold increase in sedimentation rates. Some examples are polyethylene imine, EDTA, and calcium salts. Cationic bioprocessing aids (cellulosic or polymeric) reduce pyrogen, nucleic acid, and acidic protein loads which can foul chromatography columns. The removal of these additives both during centrifugation and subsequent processing must be clearly demonstrated.

There are many different types of centrifuges, classified according to the way in which the transport of the sediment is handled. The

selection of a particular centrifuge type is determined by its capacity for handling sludge; the advantages and disadvantages of various separator types are discussed by Axelsson [in Cooney and Humphrey (eds.), op. cit., pp. 325–346]. Solids-retaining centrifuges are operated in a semibatch mode, as they must be shut down periodically to remove the accumulated solids; they are primarily used when solids concentrations are low, and have found application during the clarification and simultaneous separation of two liquids. In solids-ejecting centrifuges, the solids are removed intermittently either through radial slots or axially while the machine is running at full speed. These versatile machines can be used to handle a variety of feeds, including yeast, bacteria, mycelia, antibiotics, enzymes, and so on. Solids-discharging nozzle centrifuges have a large capacity, and can accommodate up to 30 percent solids loading. Decanter centrifuges consist of a drum, partly cylindrical and partly conical, and an internal screw conveyor for transport of the solids, which are discharged at the conical end; liquids are discharged at the cylindrical end. Levels within the drum are set by means of external nozzles.

Continuous-flow units, the scroll decanter and disk-stack centrifuges, are easiest to use from an operational perspective; shutdown of the centrifuge during the processing of a batch is not expected. While the disk-stack centrifuge enjoys popularity as a process instrument within the pharmaceutical and biotechnology industries, the precise timing of solids ejection and continuous high-speed nature of the device make for complex equipment and frequent maintenance. It is often used to harvest cells, since the solids generated are substantially wet and could lead to measurable yield losses in extracellular product systems. For intracellular product processing, the wet cell sludge is easily resuspended for use in subsequent processing.

The tubular bowl, in contrast, is a semibatch processing unit owing to the limited solids capacity of the bowl. The use of this unit requires shutdown of the centrifuge during the processing of the batch. The semibatch nature of these centrifuges can thus greatly increase processing-cycle times. The introduction of disposable sheets to act as bowl liners has significantly impacted turnaround times during processing. The dry nature of the solids generated makes the tubular-bowl centrifuge well-suited for extracellular protein processing, since losses to the cell sludge are minimal. In contrast, the dry, compact nature of the sludge can make the cells difficult to resuspend. This can be problematic for intracellular protein processing where cells are homogenized in easily clogged, mechanical disrupters.

Filtration Cross-flow filtration (microfiltration includes cross-flow filtration as one mode of operation in "Membrane Separation Processes" which appears earlier in this section) relies on the retention of particles by a membrane. The driving force for separation is pressure across a semipermeable membrane, while a tangential flow of the feed stream parallel to the membrane surface inhibits solids settling on and within the membrane matrix (Datar and Rosen, loc. cit.).

Microfiltration is used for the removal of suspended particles, recovery of cells from fermentation broth, and clarification of homogenates containing cell debris. Particles removed by microfiltration typically average greater than 500,000 nominal molecular weight [Tutunjian, in Cooney and Humphrey (eds.), op. cit., pp. 367–381; Gobler, in Cooney and Humphrey (eds.), op. cit., pp. 351–366]. Ultrafiltration focuses on the removal of low-molecular-weight solutes and proteins of various sizes, and operates in the less than 100,000 nominal-molecular-weight cutoff range [Le and Howell, in Cooney and Humphrey (eds.), op. cit., pp. 383–409]. Both operations consist of a concentration segment (of the larger particles) followed by diafiltration of the retentate [Tutunjian, in Cooney and Humphrey (eds.), op. cit., pp. 411–437].

Generally, the effectiveness of the separation is determined not by the membrane itself, but rather by the formation of a secondary or dynamic membrane caused by interactions of the solutes and particles with the membrane. The buildup of a gel layer on the surface of an ultrafiltration membrane owing to rejection of macromolecules can provide the primary separation characteristics of the membrane. Similarly, with colloidal suspensions, pore blocking and bridging of pore entries can modify the membrane performance, while molecules of size similar to the membrane pores can adsorb on the pore walls, thereby restricting passage of water and smaller solutes. Media containing poorly defined ingredients may contain suspended solids, colloidal particles, and gel-like materials that prevent effective microfiltration. In contrast to centrifugation, specific interactions can play a significant role in membrane-separation processes.

The factors to consider in the selection of cross-flow filtration include the cross-flow velocity, the driving pressure, the separation characteristics of the membrane (permeability and pore size), size of particulates relative to the membrane pore dimensions, and the hydrodynamic conditions within the flow module. Again, since particle-particle and particle-membrane interactions are key, broth conditioning (ionic strength, pH, etc.) may be necessary to optimize performance.

Selection of Cell-Separation Unit Operation The unit operation selected for cell separations can depend on the subsequent separation steps in the train. In particular, when the operation following cell separation requires cell-free feed (e.g. chromatography), filtration is used, since centrifugation is not absolute in terms of cell separation. In addition, if cells are to be stored (i.e., they contain the desired product) because later processing is more convenient (e.g., only two-shift operation, facility campaigns equipment with other products, batch is too big for single pass in equipment), it is generally better to store the cells as a frozen concentrate rather than a paste, since the concentrate thaws more completely, avoiding small granules of unfrozen cell solids that can foul homogenizers, columns, and filters. Here the retentate from filtration is desired, although the wet cell mass from a disc stack-type centrifuge may be used.

Centrifugation is generally necessary for complex media used to make natural products, for, while the media components may be sifted prior to use, they can still contain small solids that can easily foul filters. The medium to be used should be tested on a filter first to determine the fouling potential. Some types of organisms, such as filamentous organisms may sediment too slowly owing to their larger cross sections, and are better treated by filtration (mycelia have the potential to easily foul tangential-flow units; vacuum-drum filtration using a filter aid, e.g., diatomaceous earth, should also be considered). Often the separation characteristics of the broth can be improved by broth conditioning using physicochemical or biological techniques, usually of a proprietary nature.

Regardless of the machine device, centrifuges are typically maintenance-intensive. Filters can be cheaper in terms of capital and maintenance and should be considered first unless centrifugal equipment already exists. Small facilities (<1000 liters) use filtration, since centrifugation scale-down is constrained by equipment availability. Comparative economics of the two classes of operations are discussed by Datar and Rosen (loc. cit.).

Cell Disruption Intracellular protein products are present as either soluble, folded proteins or inclusion bodies. Release of folded proteins must be carefully considered. Active proteins are subject to deactivation and denaturation, and thus require the use of "gentle" conditions. In addition, due consideration must be given to the suspending medium; lysis buffers are often optimized to promote protein stability and protect the protein from proteolysis and deactivation. Inclusion bodies, in contrast, are protected by virtue of the protein agglomeration. More stressful conditions are typically employed for their release, which includes going to higher temperatures if necessary. For "native" proteins, gentler methods and temperature control are required.

The release of intracellular protein product is achieved through rupture of the cell walls, and release of the protein product to the surrounding medium, through either mechanical or nonmechanical means, or through chemical, physical, or enzymatic lysis [Engler, in Cooney and Humphrey (eds.), op. cit., pp. 305–324; Schutte and Kula, in Stephanopoulos (ed.), op. cit., pp. 505–526]. Mechanical methods use pressure, as in the Manton/APV-Gaulin/French Press, or the Microfluidizer, or mechanical grinding, as in ball mills, the latter being used typically for flocs and usually only for natural products. Nonmechanical means include use of desiccants or solvents, while cell lysis can also be achieved through physical means (osmotic shock, freeze/thaw cycles), chemical (detergents, chaotropes) or enzymatic (lysozyme, phages).

In pressure-based homogenizers, cells suspended in an aqueous

medium are forced at high velocity through a narrow, adjustable gap between a valve and its seat at pressures in excess of 50 MPa. Product release, which generally follows first-order kinetics, occurs through impingement of the high-velocity cell-suspension jet on the stationary surfaces, and possibly also by the high-shear forces generated during the acceleration of the liquid through the gap. While sufficiently high pressures can be attained using commercially available equipment to ensure good release in a single pass, the associated adiabatic temperature increases (~1.8°C/1000 psig) may cause unacceptable activity losses for heat-labile proteins. Further denaturation can occur on exposure to the lysis medium. Thus, multiple passes may be preferred, with rapid chilling of the processed-cell suspension between passes. The number of passes and the heat removal ability should be carefully optimized. The efficiency of the process depends on the homogenizing pressure and the choice of the valve unit, for which there are many designs available. Materials of construction are important to minimize erosion of the valve, to provide surface resistance to aggressive cleaning agents and disinfectants, and to permit steam cleaning and sanitization.

The release of inclusion bodies, in contrast, may follow a different strategy. Since inclusion bodies are typically recovered by centrifugation, it is often advantageous to send the lysate through the homogenizer with multiple passes to decrease the particle size of the cell debris. Since the inclusion bodies are much denser than the cell debris, the debris, now much reduced in size, can be easily separated from the inclusion bodies by centrifugation at low speeds. The inclusion bodies may be resuspended and centrifuged multiple times (often in the presence of low concentrations of denaturants) to clean up these aggregates. Since the inclusion bodies are already denatured, temperature control is not as important as in the case of native proteins.

In high-speed-agitation ball mills, cells suspended with beads are agitated by disks rotating at high speed. Ball mills have longer residence times than the pressure homogenizers, and are susceptible to channeling and shedding of the ball material.

Chemical lysis, or solubilization of the cell wall, is typically carried out using detergents such as Triton X-100, or the chaotropes urea, and guanidine hydrochloride. This approach does have the disadvantage that it can lead to some denaturation or degradation of the product. While favored for laboratory cell disruption, these methods are not typically used at the larger scales. Enzymatic destruction of the cell walls is also possible, and as more economical routes to the development of appropriate enzymes are developed, this approach could find industrial application. Again, the removal of these additives is an issue.

Physical methods such as osmotic shock, in which the cells are exposed to high salt concentrations to generate an osmotic pressure difference across the membrane, can lead to cell-wall disruption. Similar disruption can be obtained by subjecting the cells to freeze/thaw cycles, or by pressurizing the cells with an inert gas (e.g., nitrogen) followed by a rapid depressurization. These methods are not typically used for large-scale operations.

On homogenization, the lysate may drastically increase in viscosity due to DNA release. This can be ameliorated to some extent using multiple passes to reduce the viscosity. Alternatively, precipitants or nucleic acid digesting enzymes can be used to remove these viscosity-enhancing contaminants.

For postlysis processing, careful optimization must be carried out with respect to pH and ionic strength. Often it is necessary to do a buffer exchange. Cell debris can act as an ion exchanger and bind proteins ionically, thus not allowing them to pass through a filtration device or causing them to be spun out in a centrifuge. Once optimal conditions are found, these conditions can be incorporated in the lysis buffer by either direct addition (if starting from cell paste) or diafiltration (if starting from a cell concentrate).

Protein Refolding The products of recombinant DNA technology are frequently not produced in their native, biologically active form, because the foreign hosts in which they are produced lack the appropriate apparatus for the folding of the proteins. Thus, the overproduced proteins are generally recovered as refractile or inclusion bodies, or aggregates, typically 1–3 μm in size, and all cysteine residues are fully reduced. It is necessary at some stage in the processing to dissolve the aggregates and then refold them to obtain the desired biologically active product [Cleland and Wang, in Stephanopoulos (ed.), op. cit., pp. 527–555].

Advantages of inclusion bodies in the production stage are their ease of separation by centrifugation following cell disruption because of their size and density, and their provision of excellent initial-purification possibilities, as long as impurities are not co-purified to any significant extent with the inclusion bodies. They also provide a high expression level and prevent endogenous proteolysis. There can be, however, significant product loss during protein refolding to the active form.

Following cell disruption, and washing, the pellet is solubilized through the disruption of hydrogen and ionic bonds, and hydrophobic interactions by the addition of chaotropes such as guanidine hydrochloride (4–9 M), urea (7–8 M), sodium thiocyanate (4–9 M), or detergents such as Triton X-100 or sodium dodecyl sulfate. This step may also require the breaking of all incorrectly formed intramolecular disulfide bonds through the addition of appropriate reducing agents (e.g., beta mercaptoethanol). To permit proper refolding of the protein, it is necessary to reduce the chaotrope concentration either by dilution, or by solvent exchange using dialysis against a buffer (poor scale-up potential), diafiltration using the desired buffers, or electrodialysis (good scale-up potential). High-protein concentrations can lead to aggregate formation, while if the concentration is too low, the volumes to be processed become inhibitive. Subsequently, oxidation of the cysteine residues is needed to allow for correct disulfide bond formation in the native protein.

INITIAL PURIFICATION

In initial purification steps the goal is to obtain concentration with partial purification of the product, which is recovered either as a precipitate (precipitation), a solution in a second phase (liquid-liquid extraction), or adsorbed to solids (adsorption, chromatography).

Precipitation Precipitation of products, impurities or contaminants can be induced by the addition of solvents, salts, or polymers to the solution, by increasing temperature, or by adjusting the solution pH (Scopes, op. cit., pp. 41–71; Ersson et al., in Janson and Ryden, op. cit., pp. 3–32). This operation is used most often in the early stages of the separation sequence, particularly following centrifugation, filtration, and/or homogenization steps. Precipitation is often carried out in two stages, the first to remove bulk impurities and the second to precipitate and concentrate the target protein. Generally, amorphous precipitates are formed, owing to occlusion of salts or solvents, or to the presence of impurities.

Salts can be used to precipitate proteins by "salting out" effects. The effectiveness of various salts is determined by the Hofmeister series, with anions being effective in the order citrate > $PO_4^{=}$ > $SO_4^{=}$ > CH_3COO^- > Cl^- > NO_3^-, and cations according to NH_4^+ > K^+ > Na^+ (Ersson et al., op. cit., p. 10; Belter et al., op. cit., pp. 221–236). Salts should be inexpensive owing to the large quantities used in precipitation operations. Ammonium sulfate is the most commonly used precipitant. Drawbacks to this approach include low selectivity, high sensitivity to operating conditions, and downstream complications associated with salt removal and disposal of the high-nitrogen-content stream. Generally, aggregates formed on precipitation with ammonium sulfate are fragile, and are easily disrupted by shear. Thus, these precipitation operations are, following addition of salt, often aged without stirring before being fed to a centrifuge by gravity feed or using low-shear pumps (e.g., diaphragm pumps).

The organic solvents most commonly used for protein precipitation are acetone and ethanol (Ersson et al., op. cit.). These solvents can cause some denaturation of the protein product. Temperatures below 0°C can be used, since the organic solvents depress the freezing point of the water. The precipitate formed is often an extremely fine powder that is difficult to centrifuge and handle. With organic solvents, in-line mixers are preferred, as they minimize solvent-concentration gradients, and regions of high-solvent concentrations, which can lead to significant denaturation and local precipitation of undesired components typically left in the mother liquors. In general, precipitation with organic solvents at lower temperature increases yield and reduces

denaturation. It is best carried out at ionic strengths of 0.05–0.2 M.

Water-soluble polymers and polyelectrolytes (e.g., polyethylene glycol, polyethylene imine polyacrylic acid) have been used successfully in protein precipitations, and there has been some success in affinity precipitations wherein appropriate ligands attached to polymers can couple with the target proteins to enhance their aggregation. Protein precipitation can also be achieved using pH adjustment, since proteins generally exhibit their lowest solubility at their isoelectric point. Temperature variations at constant salt concentration allow for fractional precipitation of proteins.

Precipitation is typically carried out in standard cylindrical tanks with low-shear impellers. If in-line mixing of the precipitating agent is to be used, this mixing is employed just prior to the material entering the aging tank. Owing to their typically poor filterability, precipitates are normally collected using a centrifugal device.

Extraction Partitioning of the desired protein to a second phase in liquid-liquid extraction operations can be achieved using two-phase aqueous polymer systems (Albertsson, op. cit.), reversed micellar systems [Kelley and Hatton, in Stephanopoulos (ed.), op. cit., pp. 593–616], or phase-separated micellar solutions [Pryde and Phillips, *Biochem. J.*, **233,** 525–533 (1986)]. Organic solvents more typically identified with solvent-extraction operations cannot be used here because of protein solubility constraints, and because they lead to protein denaturation and degradation. Aqueous two-phase polymer systems are good for unclarified broths since particles tend to collect at the interface between the two phases, making their removal very efficient. They can also be used early on in the processing train for initial bulk-volume reduction and partial purification. These processes have not been applied widely as yet, owing both to a general lack of experience with these phase systems, and the need to remove phase-forming reagents (polymers, salts, detergents) from the products.

The basis for the separation is that when two polymers, or a polymer and certain salts, are mixed together in water, they are incompatible, leading to the formation of two immiscible but predominantly aqueous phases, each rich in only one of the two components [Albertsson, op. cit.; Kula, in Cooney and Humphrey (eds.), op. cit., pp. 451–471]. A phase diagram for a polyethylene glycol (PEG)-Dextran, two-phase system is shown in Fig. 22-85. Proteins are known to distribute unevenly between these phases. This uneven distribution can be used for the selective concentration and partial purification of the products. Partitioning between the two phases is controlled by the polymer molecular weight and concentration, protein net charge and size, and hydrophobic and electrostatic interactions. Affinity ligands covalently bonded to one of the phase-forming polymers have been found to be effective in enhancing dramatically the selectivity and partitioning behavior.

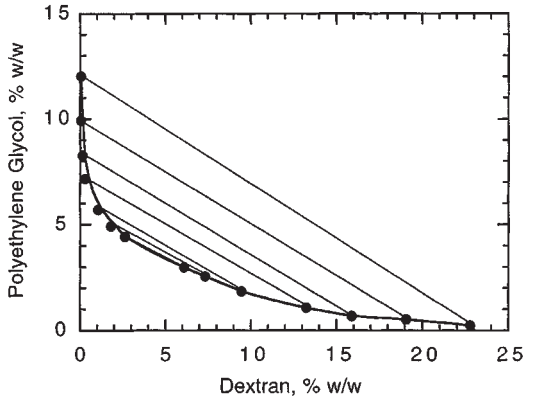


FIG. 22-85 Phase diagram for a PEG/Dextran, biphasic, aqueous-polymer system used in liquid-liquid extraction operations for protein separations. (*Albertsson,* Partition of Cell Particles and Macromolecules, *3d ed., Copyright © 1986. Reprinted by permission of John Wiley & Sons, Inc.*)

Product recovery from these systems can be accomplished by either changes in temperature or system composition. Composition changes can be affected by dilution, back extraction and micro- and ultrafiltration. As the value of the product decreases, recovery of the polymer may take on added significance. A flow diagram showing one possible configuration for the extraction and product and polymer recovery operations is shown in Fig. 22-86 [Greve and Kula, *J. Chem. Tech. Biotechnol.*, **50,** 27–42 (1991)]. The phase-forming polymer and salt are added directly to the fermentation broth. The cells or cell debris and contaminating proteins report to the salt-rich phase and are discarded. Following pH adjustment of the polymer-rich phase, more salt is added to induce formation of a new two-phase system in which the product is recovered in the salt phase, and the polymer can be recycled. In this example, disk-stack centrifuges are used to enhance the phase-separation rates. Other polymer recycling options include

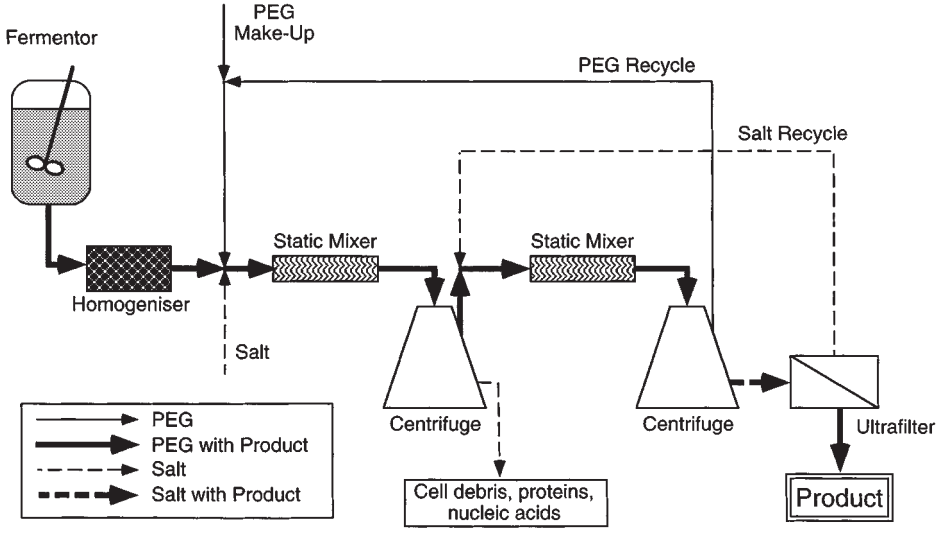


FIG. 22-86 Process scheme for protein extraction in aqueous two-phase systems for the downstream processing of intracellular proteins, incorporating PEG and salt recycling. [*Reprinted from Kelly and Hatton in Stephanopoulos (ed.), op. cit.; adapted from Greve and Kula, op. cit.*]

extraction with a solvent or supercritical fluid, precipitation, or diafiltration. Electrodialysis can be used for salt recovery and recycling.

Reversed micellar solutions can also be used for the selective extraction of proteins (Kelley and Hatton, op. cit.). In these systems, detergents soluble in an oil-phase aggregate to stabilize small water droplets having dimensions similar to those of the proteins to be separated. These droplets can host hydrophilic species such as proteins in an otherwise inhospitable organic solvent, thus enabling these organic phases to be used as protein extractants. Factors affecting the solubilization effectiveness of the solvents include charge effects, such as the net charge determined by the pH relative to the protein isoelectric point, charge distribution and asymmetry on the protein surface, and the type (anionic or cationic) of the surfactant used in the reversed micellar phase. Ionic strength and salt type affect the electrostatic interactions between the proteins and the surfactants, and also affect the sizes of the reversed micelles. Attachment of affinity ligands to the surfactants has been demonstrated to lead to enhancements in extraction efficiency and selectivity [Kelley et al., *Biotech. Bioeng.*, **42,** 1199–1208 (1993)].

Product recovery from reversed micellar solutions can often be attained by simple back extraction, by contacting with an aqueous solution having salt concentration and pH that disfavors protein solubilization, but this is not always a reliable method. Addition of cosolvents such as ethyl acetate or alcohols can lead to a disruption of the micelles and expulsion of the protein species, but this may also lead to protein denaturation. These additives must be removed by distillation, for example, to enable reconstitution of the micellar phase. Temperature increases can similarly lead to product release as a concentrated aqueous solution. Removal of the water from the reversed micelles by molecular sieves or silica gel has also been found to cause a precipitation of the protein from the organic phase.

Aqueous-detergent solutions of appropriate concentration and temperature can phase separate to form two phases, one rich in detergents, possibly in the form of micelles, and the other depleted of the detergent (Pryde and Phillips, op. cit.). Proteins distribute between the two phases, hydrophobic (e.g., membrane) proteins reporting to the detergent-rich phase and hydrophilic proteins to the detergent-free phase. Indications are that the size-exclusion properties of these systems can also be exploited for viral separations. These systems would be handled in the same way as the aqueous two-phase systems.

On occasion, for extracellular products, cell separation can be combined with an initial volume reduction and purification step using liquid-liquid extraction. This is particularly true for low-molecular-weight products, and has been used effectively for antibiotic and vitamin recovery. Often scroll decanters can be used for this separation. The solids are generally kept in suspension (which requires that the solids be denser than heavy phase), while the organic phase, which must be lighter than water (cells typically sink in water) is removed. Experience shows that scrolls are good for handling the variability seen in fermentation feedstock. Podbielniak rotating-drum extraction units have been used often, but only when solids are not sticky, gummy or flocculated, as they can get stuck in perforations of the concentric drums, but will actually give stages to the extraction in short-residence time (temperature-sensitive product). The Karr reciprocating-plate column can handle large volumes of whole-broth materials efficiently, and is amenable to ready scale-up from small laboratory-scale systems to large plant-scale equipment.

Adsorption Adsorption (see also Sec. 16: "Adsorption and Ion Exchange") can be used for the removal of pigments and nucleic acids, for example, or can be used for direct adsorption of the desired proteins. Stirred-batch or expanded-bed operations allow for presence of particulate matter, but fixed beds are not recommended for unclarified broths owing to fouling problems. These separations can be effected through charge, hydrophobic, or affinity interactions between the species and the adsorbent particles, as in the chromatographic steps outlined below. The adsorption processes described here are different from those traditionally ascribed to chromatography in that they do not rely on packed-bed operations.

In *continuous affinity recycle extraction* (CARE) operations, the adsorbent beads are added directly to the cell homogenate and the mixture is fed to a microfiltration unit. The beads loaded with the desired solute are retained by the membrane, and the product is recovered in a second stage by changing the buffer conditions to disfavor binding.

Stable expanded-bed operations promise the ability to handle whole broths efficiently, all the while maintaining plug-flow characteristics. Magnetically stabilized fluidized beds have been shown to work effectively for bioproduct separations, but are not yet used commercially. A commercially available process uses well-designed beads of appropriate densities and sizes to enable bed fluidization and stable operation without appreciable recirculation.

Membrane Processes Membrane processes are also used; diafiltration is convenient for the removal of small contaminating species such as salts and smaller proteins, and can be combined with subsequent steps to concentrate the protein. Provided that proper membrane materials have been selected to avoid protein-membrane interactions, diafiltration using ultrafiltration membranes is typically straightforward, high-yielding and capital-sparing. These operations can often tolerate the concentration of the desired protein to its solubility limit, maximizing process efficiency.

FINAL PURIFICATION AND PRODUCT FORMULATION

The final purification steps are responsible for the removal of the last traces of impurities. The volume reduction in the earlier stages of the separation train are necessary to ensure that these high-resolution operations are not overloaded. Generally, chromatography is used in these final stages. Electrophoresis can also be used, but since it is rarely found in process-scale operations, it is not addressed here. The final product preparation may require removal of solvent and drying, or lyophilization, of the product.

Chromatography Chromatography is the most widely used downstream processing operation because of its versatility, high selectivity and efficiency, in addition to its adequate scale-up potential based on wide experience in the biochemical processing industries. As familiarity is gained with other techniques such as liquid-liquid extraction they will begin to find more favor in the early stages of the separation train, but are unlikely to replace chromatography in the final stages where high purities are needed.

Chromatography is a fixed-bed adsorption operation, in which a column filled with chromatographic packing materials is fed with the mixture of components to be separated. Apart from gel-permeation chromatography, in the most commonly practiced industrial processes the solutes are adsorbed strongly to the packing materials until the bed capacity has been reached. The column may then be washed to remove impurities in the interstitial regions of the bed prior to elution of the solutes. This latter step is accomplished by using buffers or solvents which weaken the binding interaction of the proteins with the packings, permitting their recovery in the mobile phase. Different elution strategies (isocratic, gradient elution) can be used to ensure adequate separation of the species to be resolved. In gel-permeation chromatography (discussed below), and in high-performance liquid chromatography, the principle of operation is different in that it is the differential migration of the various components owing to their different affinities for the packing materials that allows the species to be separated.

Advantages of chromatography for protein separations include the large number of possible chemical interactions resulting from variations in the frequency and distribution of the amino-acid side chains on the surfaces of the proteins, and the availability of a wide array of different adsorption media. Chromatography has high efficiency and selectivity, and adequate scale-up potential.

Types of Chromatography Practiced Separation of proteins using chromatography can exploit a range of different physical and chemical properties of the proteins and the chromatography adsorption media [Janson and Ryden, op. cit.; Scopes, op. cit.; Egerer, in Finn and Prave (eds.), *Biotechnology Focus 1,* Hanser Publishers, Munich, 1988, pp. 95–151]. Parameters that must be considered in the selection of a chromatographic method include composition of the reaction mixture, the chemical structure and stability of the components, the electric charge at a defined pH value and the isoelectric point of the proteins, the hydrophilicity and hydrophobicity of the

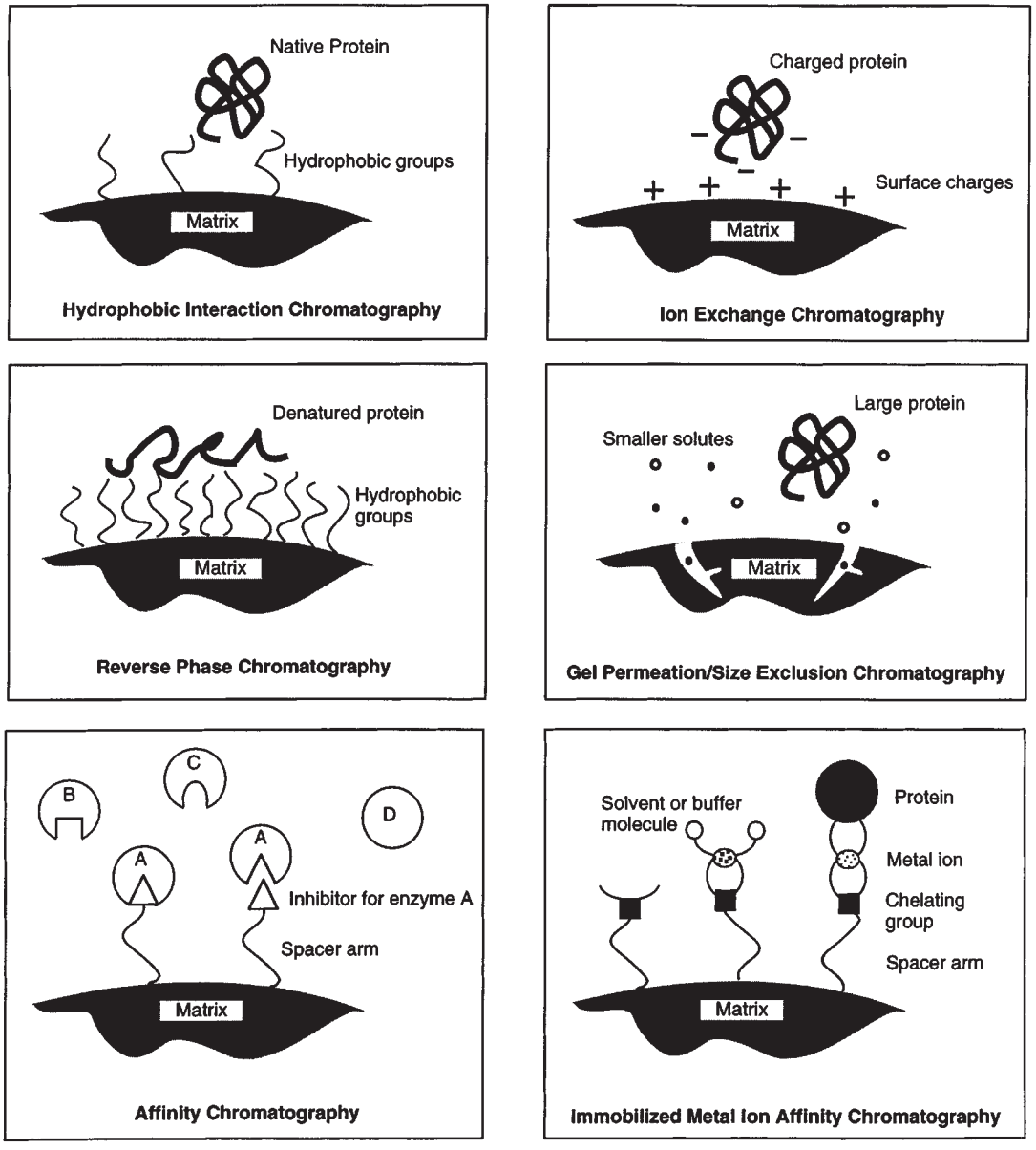


FIG. 22-87 Schematic illustration of the chromatographic methods most commonly used in downstream processing for protein recovery.

components, and molecular size. The different types of interactions are illustrated schematically in Fig. 22-87.

Ion-exchange chromatography relies on the coulombic attraction between the ionized functional groups of proteins and oppositely charged functional groups on the chromatographic support. It is used to separate the product from contaminating species having different charge characteristics under well-defined eluting conditions, and for concentration of the product, owing to the high-adsorptive capacity of most ion-exchange resins, and the resolution attainable. It is used effectively at the front end of a downstream processing train for early volume reduction and purification.

The differences in sizes and locations of hydrophobic pockets or patches on proteins can be exploited in *hydrophobic interaction chromatography* (HIC) and *reversed-phase chromatography* (RPC); discrimination is based on interactions between the exposed hydrophobic residues and hydrophobic ligands which are distributed evenly throughout an hydrophilic porous matrix. As such, the binding characteristics complement those of other chromatographic methods, such as ion-exchange chromatography.

In HIC, the hydrophobic interactions are relatively weak, often driven by salts in moderate concentration (1 to 2 M), and depend primarily on the exposed residues on or near the protein surface; preservation of the native, biologically active state of the protein is an important feature of HIC. Elution can be achieved differentially by decreasing salt concentration or increasing the concentration of polarity perturbants (e.g., ethylene glycol) in the eluent.

Reversed-phase chromatography relies on significantly stronger hydrophobic interactions than in HIC, which can result in unfolding and exposure of the interior hydrophobic residues, i.e., leads to protein denaturation and irreversible inactivation; as such, RPC depends

on total hydrophobic-residue content. Elution is effected by organic solvents applied under gradient conditions.

Ligands for both HIC and RPC are straight chain alkanes or simple aromatic compounds. Increasing the carbon number and the graft density of the ligands on the support surface leads to increasing strength of interaction and passing from HIC to RPC mode of operation. Raising the temperature increases the hydrophobic interactions at the temperatures commonly encountered in biological processing.

HIC is most effective during the early stages of a purification strategy and has the advantage that sample pretreatment such as dialysis or desalting after salt precipitation is not usually required. It is also finding increased use as the last high-resolution step to replace gel filtration. It is a group-separation method, and generally 50 percent or more of extraneous impurities are removed. This method is characterized by high-adsorption capacity, good selectivity, and satisfactory yield of active material.

Despite the intrinsically nonspecific nature of ion-exchange and reversed-phase/hydrophobic interactions, it is often found that chromatographic techniques based on these interactions can exhibit remarkable resolution; this is attributed to the dynamics of multisite interactions being different for proteins having differing surface distributions of hydrophobic and/or ionizable groups.

Gel-permeation chromatography separates proteins nominally on the basis of size only, where the effective size of the protein is determined by its geometry and solvation characteristics. Smaller proteins are able to penetrate the pore volumes of the beads, and are therefore retained relative to the larger proteins, which remain in the fast-flowing fluid in the interstitial regions of the bed. Such ideal behavior is rarely observed, however, as proteins can interact adsorptively with the gel matrix, thus affecting their relative elution behaviors. Industrially, gel-permeation chromatography is used for desalting, removing low-molecular-weight impurities, and removal of desired product oligomers. It is used in the latter stages of the separation sequence, often as a final "polishing" step.

Protein affinity chromatography can be used for the separation of an individual compound, or a group of structurally similar compounds from crude-reaction mixtures, fermentation broths, or cell lysates by exploiting very specific and well-defined molecular interactions between the protein and affinity groups immobilized on the packing-support material. Examples of affinity interactions include antibody-antigen, hormone-receptor, enzyme-substrate/analog/inhibitor, metal ion-ligand, and dye-ligand pairs. Monoclonal antibodies are particularly effective as biospecific ligands for the purification of pharmaceutical proteins. Affinity chromatography may be used for the isolation of a pure product directly from crude fermentation mixtures in a single chromatographic step. Immunosorbents should not be subjected to crude extracts, however, as they are particularly susceptible to fouling and inactivation. Affinity chromatography does not find wide use on the process scale because of its high cost, if a protein ligand such as A or G is to be used.

Immobilized metal ion affinity chromatography (IMAC) relies on the interaction of certain amino-acid residues, particularly histidine, cysteine, and tryptophan, on the surface of the protein with metal ions fixed to the support by chelation with appropriate chelating compounds, invariably derivatives of iminodiacetic acid. Commonly-used metal ions are Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}. Despite its relative complexity in terms of the number of factors which influence the process, IMAC is beginning to find industrial applications. The choice of chelating group, metal ion, pH, and buffer constituents will determine the adsorption and desorption characteristics. Elution can be effected by several methods, including pH gradient, competitive ligands, organic solvents, and chelating agents.

Following removal of unbound materials in the column by washing, the bound substances are recovered by changing conditions to favor desorption. A gradient or stepwise reduction in pH is often suitable. Otherwise, one can use competitive elution with a gradient of increasing concentration. IMAC eluting agents include ammonium chloride, glycine, histamine, histidine, or imidazol. Inclusion of a chelating agent such as EDTA in the eluent will allow all proteins to be eluted indiscriminately along with the metal ion.

Chromatographic Development The basic concepts of chromatographic adsorption separations are described elsewhere in this handbook. Proteins differ from small solutes in that the large number of charged and/or hydrophobic residues on the protein surface provide multiple binding sites, which ensure stronger binding of the proteins to the adsorbents, as well as some discrimination based on the surface distribution of amino-acid residues. The proteins are recovered by elution with a buffer that reduces the strength of this binding and permits the proteins to be swept out of the column with the buffer solution. In isocratic elution, the buffer concentration is maintained constant during the elution period. Since the different proteins may have significantly different adsorption isotherms, the recovery may not be complete, or it may take excessive processing time to recover all proteins from the column. In gradient elution operations, the composition of the mobile phase is changed during the process to decrease the binding strength of the proteins successively, the more loosely bound proteins being removed first before the eluent is strengthened to enable recovery of the more strongly adsorbed species. The change in eluent composition can be gradual and continuous, or it can be stepwise. Industrially, in large-scale columns it is difficult to maintain a continuous gradient owing to difficulties in fluid distribution, and thus stepwise changes are almost universally used. In some adsorption modes, the protein can be recovered by the successive addition of competing compounds to displace the adsorbed proteins. In all cases, the product is eluted as a Gaussian (to a first approximation) peak, with some possible overlap between adjacent product peaks.

Displacement chromatography relies on a different mode of elution. Here a displacer which is more strongly adsorbed than any of the proteins is introduced with the mobile phase. As the displacer concentration front develops, it pushes the proteins ahead of itself. The more strongly adsorbed proteins then act as displacers for the less strongly bound proteins, and so on. This leads to the development of a displacer train in which the different molecules are eluted from the column in abutting rectangular peaks in the order of their interaction strength with the adsorption sites of the column. Despite its apparent process advantages, displacement chromatography has not yet become an accepted industrial operation, primarily because of lack of suitable displacers, and possible contamination of the protein product with these displacers.

For efficient adsorption it is advisable to equilibrate both the column and the sample with the optimum buffer for binding. Prior to this, the column must be cleaned to remove tightly bound impurities by increasing the salt concentration beyond that used in the product-elution stages. At the finish of cleaning operation the column should be washed with several volumes of the starting buffer to remove remaining adsorbed material. In desorption, it is necessary to drive the favored binding equilibrium for the adsorbed substance from the stationary to the mobile phase. Ligand-protein interactions are generally a combination of electrostatic, hydrophobic, and hydrogen bonds, and the relative importance of each of these and the degree of stability of the bound protein must be considered in selecting appropriate elution conditions; frequently compromises must be made. Gradient elution often gives good results.

Changes in pH or ionic strength are generally nonspecific in elution performance; ionic-strength increases are effective when the protein binding is predominantly electrostatic, as in IEC. Polarity changes are effective when hydrophobic interactions play the primary role in protein binding. By reducing the polarity of the eluting mobile phase, this phase becomes a more thermodynamically favorable environment for the protein than adsorption to the packing support. A chaotropic salt (KSCN, KCNO, KI in range 1–3 M) or denaturing agent (urea, guanidine HCl; 3–4 M) in the buffer can also lead to enhanced desorption. For the most hydrophobic proteins (e.g., membrane proteins) one can use detergents just below their critical micelle concentrations to solubilize the proteins and strip them from the packing surface.

Specific elution requires more selective eluents. Proteins can be desorbed from ligands by competitive binding of the eluting agent (low concentration 5–100 mM) either to the ligand or to the protein. Specific eluents are most frequently used with group-specific adsorbents since selectivity is greatly increased in the elution step. The effectiveness of the elution step can be tailored using a single eluent, pulses of different eluents, or eluent gradients. These systems are

generally characterized by mild desorption conditions. If the eluting agent is bound to the protein, it can be dissociated by desalting on a gel-filtration column or by diafiltration.

Column Packings The quality of the separation obtained in chromatographic separations will depend on the capacity, selectivity, and hydraulic properties of the stationary phase, which usually consists of porous beads of hydrophilic polymers filled with the solvent. The xerogels (e.g., cross-linked dextran) shrink and swell depending on solvent conditions, while aerogels have sizes independent of solution conditions. A range of materials is used for the manufacture of gel beads, classified according to whether they are inorganic, synthetic, or polysaccharides. The most widely used materials are based on neutral polysaccharides and polyacrylamide. Cellulose gels, such as cross-linked dextran, are generally used as gel-filtration media, but can also be used as a matrix for ion exchangers. The primary use of these gels is for desalting and buffer exchange of protein solutions, as nowadays, fractionation by gel filtration is performed largely with composite gel matrices. Agarose, a low-charge fraction of the seaweed polysaccharide agar, is a widely used packing material.

Microporous gels made by point cross-linking dextran or polyacrylamides are used for molecular-sieve separations such as size-exclusion chromatography and gel filtration, but are generally too soft at the porosities required for efficient protein chromatography. Macroporous gels are most often obtained from aggregated and physically cross-linked polymers. Examples include agarose, macroreticular polyacrylamide, silica, and synthetic polymers. These gels are good for ion-exchange and affinity chromatography, as well as for other adsorption chromatography techniques. Composite gels, in which the microporous gel is introduced into the pores of macroreticular gels, combine the advantages of both types.

High matrix rigidity is offered by porous silica, which can be derivatized to enhance its compatibility with proteins, but it is unstable at alkaline pH. Hydroxyapatite particles have high selectivity for a wide range of proteins and nucleic acids.

Sequencing of Chromatography Steps The sequence of chromatographic steps used in a protein purification train should be designed such that the more robust techniques are used first, to obtain some volume reduction (concentration effect) and to remove major impurities that might foul subsequent units; these robust units should have high chemical and physical resistance to enable efficient regeneration and cleaning, and should be of low material cost. These steps should be followed by the more sensitive and selective operations, sequenced such that buffer changes and concentration steps between applications to chromatographic columns are avoided. Frequently, ion-exchange chromatography is used as the first step. The elution peaks from such columns can be applied directly to hydrophobic-interaction chromatographic columns or to a gel-filtration unit, without the need for desalting of the solution between applications. These columns can also be used as desalting operations, and the buffers used to elute the columns can be selected to permit direct application of the eluted peaks to the next chromatographic step.

Factors to be considered in making the selection of chromatography processing steps are cost, sample volume, protein concentration and sample viscosity, degree of purity of protein product, presence of nucleic acids, pyrogens, and proteolytic enzymes. Ease with which different types of adsorbents can be washed free from adsorbed contaminants and denatured proteins must also be considered.

Lyophilization and Drying After the last high-performance purification steps it is usually necessary to prepare the finished product for special applications. For instance, final enzyme products are often required in the form of a dry powder to provide for stability and ease of handling, while pharmaceutical preparations also require high purity, stability during formulation, absence of microbial load, and extended shelf life. This product-formulation step may involve drying of the final products by freeze drying, spray drying, fluidized-bed drying, or crystallization (Golker, in Stephanopoulos, op. cit., pp. 695–714).

Freeze drying, or lyophilization, is normally reserved for temperature-sensitive materials such as vaccines, enzymes, microorganisms, and therapeutic proteins, as it can account for a significant portion of total production cost. This process is characterized by three distinct steps, beginning with freezing of the product solution, followed by water removal by sublimation in a primary drying step, and ending with secondary drying by heating to remove residual moisture.

Freezing is carried out on cooled plates in trays or with the product distributed as small particles on a drum cooler; by dropping the product solution in liquid nitrogen or some other cooling liquid; by cospraying with liquid CO_2 or liquid nitrogen; or by freezing with circulating cold air. The properties of the freeze-dried product, such as texture and ease of rehydration, depend on the size and shape of the ice crystals formed, which in turn depend on the degree of undercooling. It is customary to cool below the lowest equilibrium eutectic temperature of the mixture, although many multicomponent mixtures do not exhibit eutectic points. Freezing should be rapid to avoid effects from local concentration gradients. Removal of water from solution by the formation of ice crystals leads to changes in salt concentration and pH, as well as enhanced concentration of the product, in the remaining solution; this in turn can enhance reaction rates, and even reaction order can change, resulting in cold denaturation of the product. With a high initial protein concentration the freeze concentration factor and the amount of ice formed will be reduced, resulting in greater product stability. For aseptic processing, direct freezing in the freeze-drying plant ensures easier loading of the solution after filtration than if transferred separately from remote freezers.

In the primary drying step, heat of sublimation is supplied by contact, conduction, or radiation to the sublimation front. It is important to avoid partial melting of the ice layer. Many pharmaceutical preparations dried in ampoules are placed on heated shelves. The drying time depends on the quality of ice crystals, indicating the importance of controlling the freezing process; smaller crystals offer higher interfacial areas for heat and mass transfer, but larger crystals provide pores for diffusion of vapor away from the sublimation front.

A high percentage of water remains after the sublimation process, present as adsorbed water, water of hydration or dissolved in the dry amorphous solid; this is difficult to remove. Usually, shelf-temperature is increased to 25 to 40°C and chamber pressure is lowered as far as possible. This still does not result in complete drying, however, which can be achieved only by using even higher temperatures, at which point thermally induced product degradation can occur.

Excipients can be used to improve stability and prevent deterioration and inactivation of biomolecules through structural changes such as dissociation from multimeric states into subunits, decrease in α-helical content accompanied by an increase in β-sheet structure, or complete unfolding of helical structure. These are added prior to the freeze-drying process. Examples of these protective agents include sugars, sugar derivatives, and various amino acids, as well as polymers such as dextran, polyvinyl pyrrolidone, hydroxyethyl starch, and polyethylene glycol. Some excipients, the **lyoprotectants,** provide protection during freezing, drying, and storage, while others, the **cryoprotectants,** offer protection only during the freezing process.

Spray drying can use up to 50 percent less energy than freeze-drying operations and finds application in the production of enzymes used as industrial catalysts, as additives for washing detergents, and as the last step in the production of single-cell protein. The product is usually fed to the dryer as a solution, a suspension, or a free-flowing wet substance. Spray drying is an adiabatic process, the energy being provided by hot gas (usually hot air) at temperatures between 120 and 400°C. Product stability is assured by a very short drying time in the spray-drying equipment, typically in the subsecond to second range, which limits exposure to the elevated temperatures in the dryer. Protection can be offered by addition of additives (e.g., galactomannan, polyvinyl pyrrolidone, methyl cellulose, cellulose).

The spray-drying process requires dispersion of the feed as small droplets to provide a large heat and mass-transfer area. The dispersion of liquid is attained using rotating disks, different types of nozzles or ultrasound, and is affected by interfacial tension, density, and dynamic viscosity of the feed solution, as well as the temperature and relative velocities of the liquid and air in the mixing zone. Rotating-disk atomizers operate at 4000 to 50,000 rpm to generate the centrifugal forces needed for dispersion of the liquid phase; typical droplet sizes of 25 to

950 μm are obtained. These atomizers are specially suitable for dispersing suspensions that would tend to clog nozzles.

For processing under aseptic conditions, the spray drier must be connected to a filling line that allows aseptic handling of the product.

INTEGRATION OF FERMENTATION AND DOWNSTREAM PROCESSING OPERATIONS

Traditionally, the upstream fermentation and cell culture processes have been viewed as being distinct from the subsequent downstream processing and purification steps, and the two different sets of processes have been optimized individually. In some instances, careful consideration of the conditions used in the fermentation process, or manipulation of the genetic makeup of the host, can simplify and even eliminate some unit operations in the downstream processing sequence [Kelley and Hatton, *Bioseparation,* **1,** 303–349 (1991)]. Some of the advances made in this area are the engineering of strains of *Escherichia coli* to allow the inducible expression of lytic enzymes capable of disrupting the wall from within for the release of intracellular protein products, the use of secretion vectors for the expression of proteins in bacterial production systems, and protein synthesis to include a peptide or protein fusion to confer unique properties to the product to facilitate subsequent downstream processing. The cell culture medium can be selected to avoid components that can hinder subsequent purification procedures. Integration of the fermentation and initial separation/purification steps in a single operation can also lead to enhanced productivity, particularly when the product can be removed as it is formed to prevent its proteolytic destruction by the proteases which are frequently the by-product of fermentation processes. The introduction of a solvent directly to the fermentation medium (e.g., phase-forming polymers), the continuous removal of products using ultrafiltration membranes, or the use of continuous fluidized-bed operations are examples of this integration.

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Section 23

Chemical Reactors

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Nomenclature and Units

Following is a listing of typical nomenclature and units expressed in SI and U.S. customary. Specific definitions and units are stated at the place of application in the section.

Symbol	Definition	SI units	U.S. customary units
A, B, C, . . .	Names of substances, or their concentrations		
A^0	Free radical, as CH_j^0		
C_a	Concentration of substance A	kg mol/m^3	lb mol/ft^3
C^0	Initial mean concentration in vessel	kg mol/m^3	lb mol/ft^3
C_p	Heat capacity	kJ/(kg·K)	Btu/(lbm·°F)
CSTR	Continuous stirred tank reactor		
D, D_e, D_x	Dispersion coefficient	m^2/s	ft^2/s
D_{eff}	Effective diffusivity	m^2/s	ft^2/s
D_K	Knudsen diffusivity	m^2/s	ft^2/s
$E(t)$	Residence time distribution		
$E(t_r)$	Normalized residence time distribution		
f_a	C_a/C_{a0} or n_a/n_{a0}, fraction of A remaining unconverted		
$F(t)$	Age function of tracer		
ΔG	Gibbs energy change	kJ	Btu
Ha	Hatta number		
ΔH_r	Heat of reaction	kJ/kg mol	Btu/lb mol
K, K_c, K_y, K_ϕ	Chemical equilibrium constant		
k, k_c, k_p	Specific rate of reaction	Variable	Variable
L	Length of path in reactor	m	ft
n	Parameter of Erlang or gamma distribution, or number of stages in a CSTR battery		
n_a	Number of mols of A present		
n_a'	Number of mols flowing per unit time, the prime (′) may be omitted when context is clear		
n_t	Total number of mols		
p_a	Partial pressure of substance A	kPa	psi
Pe	Peclet number for dispersion		
PFR	Plug flow reactor		
Q	Heat transfer	kJ	Btu
r	Radial position	m	ft
r_a	Rate of reaction of A per unit volume	Variable	Variable
R	Radius of cylindrical vessel	m	ft
Re	Reynolds number		
Sc	Schmidt number		

Symbol	Definition	SI units	U.S. customary units
t	Time	s	s
$\bar{t}$	Mean residence time	s	s
t_r	$t/\bar{t}$, reduced time		
TFR	Tubular flow reactor		
u	Linear velocity	m/s	ft/s
$u(t)$	Unit step input		
V	Volume of reactor contents	m^3	ft^3
V'	Volumetric flow rate	m^3/s	ft^3/s
V_r	Volume of reactor	m^3	ft^3
x	Axial position in a reactor	m	ft
x_a	$1 - f_a = 1 - C_a/C_{a0}$ or $1 - n_a$, n_{a0}, fraction of A converted		
z	x/L, normalized axial position		
	Greek letters		
β	r/R, normalized radial position		
$\gamma^3(t)$	Skewness of distribution		
$\delta(t)$	Unit impulse input, Dirac function		
ε	Fraction void space in a packed bed		
ϑ	$t/\bar{t}$, reduced time		
η	Effectiveness of porous catalyst		
$\Lambda(t)$	Intensity function		
μ	Viscosity	Pa·s	lbm/(ft·s)
ν	v/ρ, kinematic viscosity	m^2/s	ft^2/s
π	Total pressure	Pa	psi
ρ	Density	kg/m^3	lbm/ft^3
ρ	r/R, normalized radial position in a pore		
$\sigma^2(t)$	Variance		
$\sigma^2(t_r)$	Normalized variance		
τ	$t/\bar{t}$, reduced time		
τ	Tortuosity		
ϕ	Thiele modulus		
ϕ_m	Modified Thiele modulus		
	Subscripts		
0	Subscript designating initial or inlet conditions, as in C_{a0}, n_{a0}, V_0'', . . .		

MODELING CHEMICAL REACTORS

General References: The General References listed in Sec. 7 are applicable for Sec. 23. References to specific topics are made throughout this section.

An industrial chemical reactor is a complex device in which heat transfer, mass transfer, diffusion, and friction may occur along with chemical reaction, and it must be safe and controllable. In large vessels, questions of mixing of reactants, flow distribution, residence time distribution, and efficient utilization of the surface of porous catalysts also arise. A particular process can be dominated by one of these factors or by several of them; for example, a reactor may on occasion be predominantly a heat exchanger or a mass-transfer device. A successful commercial unit is an economic balance of all these factors.

Some modes of heat transfer to stirred tank reactors are shown in Fig. 23-1 and to packed bed reactors in Fig. 23-2. Temperature and composition profiles of some processes are shown in Fig. 23-3. Operating data, catalysts, and reaction times are stated for a number of industrial reaction processes in Table 23-1.

Many successful types of reactors are illustrated throughout this section. Additional sketches may be found in other books on this topic, particularly in Walas (*Chemical Process Equipment Selection and Design*, Butterworths, 1990) and Ullmann (*Encyclopedia of Chemical Technology* (in German), vol. 3, Verlag Chemie, 1973, pp. 321–518).

The general characteristics of the main types of reactors—batch and continuous—are clear. Batch processes are suited to small production rates, to long reaction times, or to reactions where they may have superior selectivity, as in some polymerizations. They are conducted in tanks with stirring of the contents by internal impellers, gas bubbles, or pumparound. Temperature control is with internal surfaces or jackets, reflux condensers, or pumparound through an exchanger.

Large daily production rates are mostly conducted in continuous equipment, either in a series of stirred tanks or in units in which some degree of plug flow is attained. Many different equipment configurations are illustrated throughout this section for reactions of liquids, gases, and solids, singly or in combinations. By showing how something has been done previously, this picture gallery may suggest how a similar new process could be implemented.

Continuous stirred tank reactors (CSTRs) are frequently employed multiply and in series. Reactants are continuously fed to the first vessel; they overflow through the others in succession, while being thoroughly mixed in each vessel. Ideally, the composition is uniform in individual vessels, but a stepped concentration gradient exists in the system as a whole. For some cases, a series of five or six vessels approximates the performance of a plug flow reactor. Instead of being in distinct vessels, the several stages of a CSTR battery can be put in a single shell. If horizontal, the multistage reactor is compartmented by vertical weirs of different heights, over which the reacting mixture cascades. When the reactants are of limited miscibilities and have a sufficient density difference, the vertical staged reactor lends itself to countercurrent operation, a real advantage with reversible reactions. A small fluidized bed is essentially completely mixed. A large commercial fluidized bed reactor is of nearly uniform temperature, but the flow patterns consist of mixed and plug flow and in-between zones.

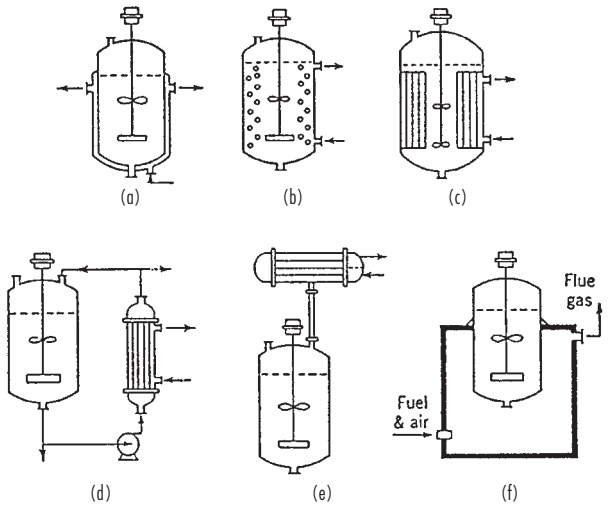


FIG. 23-1 Heat transfer to stirred tank reactors. (*a*) Jacket. (*b*) Internal coils. (*c*) Internal tubes. (*d*) External heat exchanger. (*e*) External reflux condensor. (*f*) Fired heater. (*Walas,* Reaction Kinetics for Chemical Engineers, *McGraw-Hill, 1959*).

Tubular flow reactors (TFRs) are characterized by continuous gradients of concentration in the direction of flow that approach plug flow, in contrast to the stepped gradient characteristic of the CSTR battery. They may have several pipes or tubes in parallel. The reactants are charged continuously at one end and products are removed at the other end. Normally a steady state is attained, a fact of importance for automatic control and for laboratory work. Both horizontal and vertical orientations are common. When heat transfer is needed, individual tubes are jacketed or shell-and-tube construction is used. In the latter case the reactants may be on either the shell or the tube side. The reactant side may be filled with solid particles, either catalytic (if required) or inert, to improve heat transfer by increased turbulence or to improve interphase contact in heterogeneous reactions. Large-diameter vessels with packing or trays may approach plug flow behavior and are widely employed. Some of the configurations in use are axial flow, radial flow, multiple shell, with built-in heat exchangers, horizontal, vertical and so on. *Quasi-plug flow reactors* have continuous gradients but are not quite in plug flow.

Semiflow or batch flow operations may employ a single stirred tank or a series of them. Some of the reactants are loaded into the reactors as a single charge and the remaining ones are then fed gradually. This mode of operation is especially favored when large heat effects occur and heat-transfer capability is limited, since exothermic reactions can be slowed down and endothermic rates maintained by limiting the concentrations of some of the reactants. Other situations making this sort of operation desirable occur when high concentrations may result in the formation of undesirable side products, or when one of the reactants is a gas of limited solubility so that it can be fed only at the dissolution rate.

Relative advantages and fields of application of continuous stirred and plug flow reactors may be indicated briefly. A reaction battery is a highly flexible device, although both mechanically and operationally more expensive and complex than tubular units. Relatively slow reactions are best conducted in a CSTR battery, which is usually cheaper than a single reactor for moderate production rates. The tubular reactor is especially suited to cases needing considerable heat transfer, where high pressures and very high or very low temperatures occur, and when relatively short reaction times suffice.

MATHEMATICAL MODELS

A model of a reaction process is a set of data and equations that is believed to represent the performance of a specific vessel configuration (mixed, plug flow, laminar, dispersed, and so on). The equations include the stoichiometric relations, rate equations, heat and material balances, and auxiliary relations such as those of mass transfer, pressure variation, contacting efficiency, residence time distribution, and so on. The data describe physical and thermodynamic properties and, in the ultimate analysis, economic factors.

Correlations of heat and mass-transfer rates are fairly well developed and can be incorporated in models of a reaction process, but the chemical rate data must be determined individually. The most useful rate data are at constant temperature, under conditions where external mass transfer resistance has been avoided, and with small particles

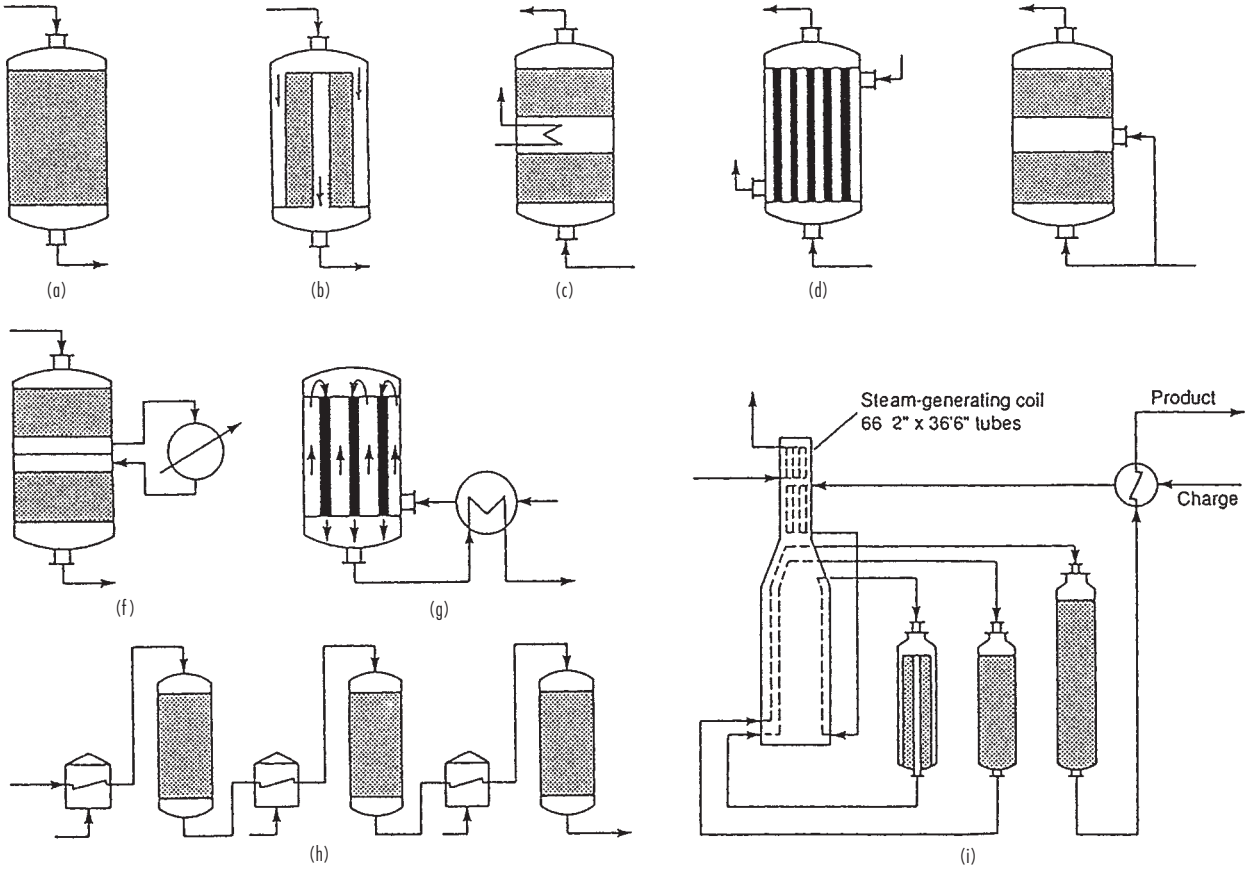


FIG. 23-2 Heat exchange in packed reactors. (*a*) Adiabatic downflow. (*b*) Adiabatic radial flow, low ΔP. (*c*) Built-in interbed exchanger. (*d*) Shell and tube. (*e*) Interbed cold-shot injection. (*f*) External interbed exchanger. (*g*) Autothermal shell, outside influent/effluent heat exchanger. (*h*) Multibed adiabatic reactors with interstage heaters. (*i*) Platinum catalyst, fixed bed reformer for 5,000 BPSD charge rate; reactors 1 and 2 are 5.5 by 9.5 ft and reactor 3 is 6.5 by 12.0 ft; temperatures 502 ⇒ 433, 502 ⇒ 471, 502 ⇒ 496°C. To convert ft to m, multiply by 0.3048; BPSD to m^3/h, multiply by 0.00662.

with complete catalyst effectiveness. Equipment for obtaining such data is now widely used, especially for reactions with solid catalysts, and it is virtually essential for serious work. Simpler equipment gives data that are more difficult to interpret but may be adequate for exploratory work.

Once fundamental data have been obtained, the goal is to develop a mathematical model of the process and to utilize it to explore such possibilities as product selectivity, start-up and shut-down behavior, vessel configuration, temperature, pressure, and conversion profiles, and so on.

How complete a model has to be is an open question. Very elaborate ones are justifiable and have been developed only for certain widely practiced and large-scale processes, or for processes where operating conditions are especially critical. The only policy to follow is to balance the cost of development of the model against any safety factors that otherwise must be applied to a final process design. Engineers constantly use heat and material balances without perhaps realizing, like Moliere's Bourgeois, that they are modeling mathematically. The simplest models may be adequate for broad discrimination between alternatives.

MODELING PRINCIPLES

How a differential equation is formulated for some kinds of ideal reactors is described briefly in Sec. 7 of this Handbook and at greater length with many examples in Walas (*Modeling with Differential Equations in Chemical Engineering,* Butterworth-Heineman, 1991). First, a mechanism is assumed: whether completely mixed, plug flow, laminar, with dispersion, with bypass or recycle or dead space, steady or unsteady, and so on. Then, for a differential element of space and/or time the elements of a conservation law,

$$\text{Inputs} + \text{Sources} = \text{Outputs} + \text{Sinks} + \text{Accumulations}$$

are formulated and put together. Any transport properties are introduced through known correlations together with the parameters of specified rate equations. The model can be used to find the performance under various conditions, or its parameters can be evaluated from experimental data. The two comprehensive examples in this section evaluate performance when all the parameters are known. There are other examples in these sections where the parameters of rate equations, residence time distributions, or effectiveness are to be found from rate or tracer data.

CHEMICAL KINETIC LAWS

The two basic laws of kinetics are the *law of mass action* for the rate of a reaction and the *Arrhenius equation* for its dependence on temperature. Both of these are strictly empirical. They depend on the structures of the molecules, but at present the constants of the equations cannot be derived from the structures of reacting molecules. For a reaction, $aA + bB \Rightarrow$ Products, the combined law is

$$r_a = -\frac{1}{V_r}\frac{dn_a}{dt} = \exp\left(\gamma + \frac{\delta}{T}\right) C_a^{\alpha} C_b^{\beta} \qquad (23\text{-}1)$$

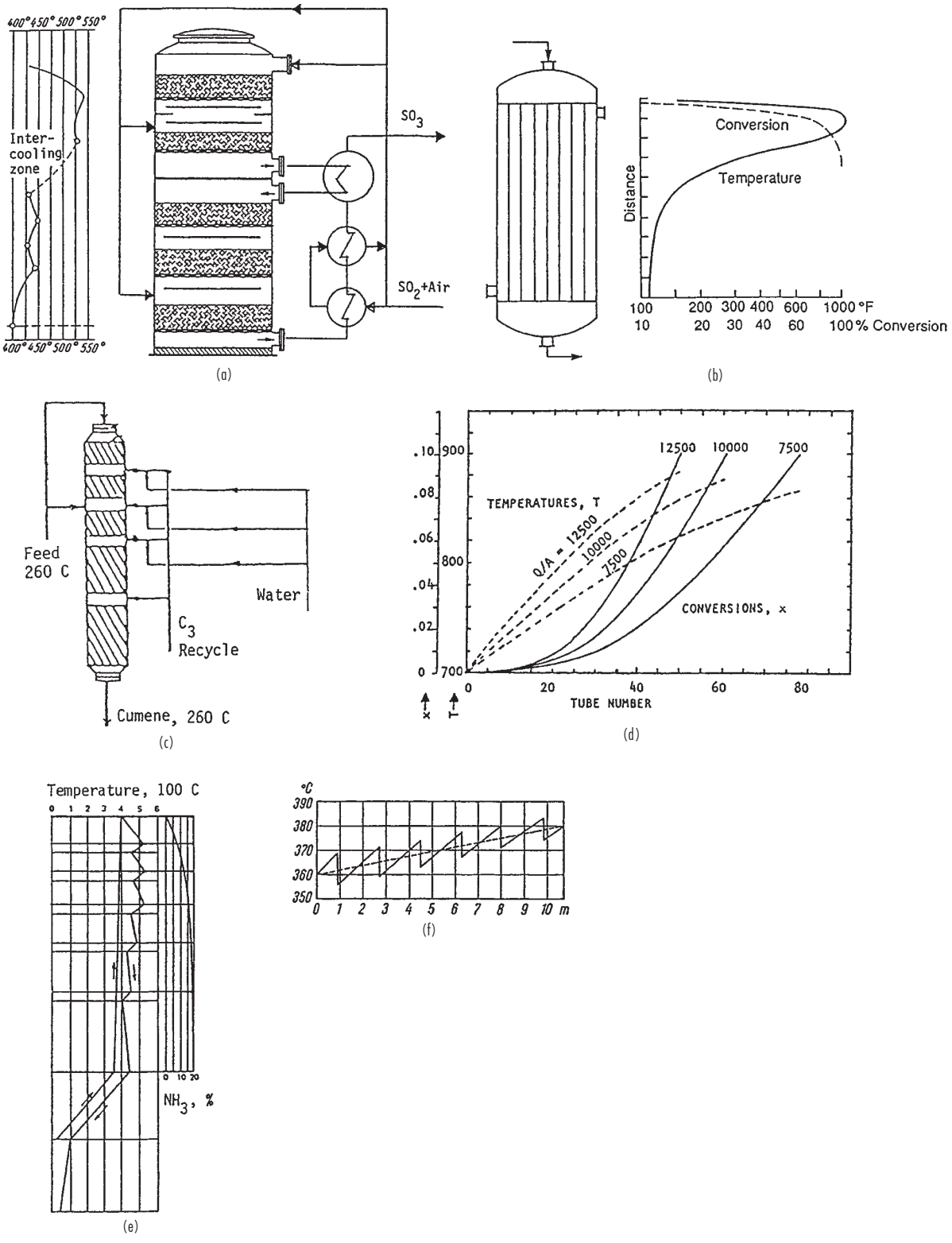


FIG. 23-3 Temperature and composition profiles. (*a*) Oxidation of SO_2 with intercooling and two cold shots. (*b*) Phosgene from CO and Cl_2, activated carbon in 2-in tubes, water cooled. (*c*) Cumene from benzene and propylene, phosphoric acid on quartz, with four quench zones, 260°C. (*d*) Mild thermal cracking of a heavy oil in a tubular furnace, back pressure of 250 psig and several heat fluxes, Btu/(ft²·h), *T* in °F. (*e*) Vertical ammonia synthesizer at 300 atm, with five cold shots and an internal exchanger. (*f*) Vertical methanol synthesizer at 300 atm, Cr_2O_3-ZnO catalyst, with six cold shots totaling 10 to 20 percent of the fresh feed. To convert psi to kPa, multiply by 6.895; atm to kPa, multiply by 101.3.

TABLE 23-1 Residence Times and/or Space Velocities in Industrial Chemical Reactors*

Product (raw materials)	Type	Reactor phase	Catalyst	*T*, °C	*P*, atm	Residence time or space velocity	Source and page†
Acetaldehyde (ethylene, air)	FB	L	Cu and Pd chlorides	50–100	8	6–40 min	[2] 1, [7] 3
Acetic anhydride (acetic acid)	TO	L	Triethylphosphate	700–800	0.3	0.25–5 s	[2]
Acetone (*i*-propanol)	MT	LG	Ni	300	1	2.5 h	[1] 1 314
Acrolein (formaldehyde, acetaldehyde)	FL	G	MnO, silica gel	280–320	1	0.6 s	[1] 1 384, [7] 33
Acrylonitrile (air, propylene, ammonia)	FL	G	Bi phosphomolybdate	400	1	4.3 s	[3] 684, [2] 47
Adipic acid (nitration of cyclohexanol)	TO	L	Co naphthenate	125–160	4–20	2 h	[2] 51, [7] 49
Adiponitrile (adipic acid)	FB	G	H_3BO_3 H_3PO_4	370–410	1	3.5–5 s 350–500 GHSV	[1] 2 152, [7] 52
Alkylate (*i*-C_4, butenes)	CST	L	H_2SO_4	5–10	2–3	5–40 min	[4] 223
Alkylate (*i*-C_4, butenes)	CST	L	HF	25–38	8–11	5–25 min	[4] 223
Allyl chloride (propylene, Cl_2)	TO	G	NA	500	3	0.3–1.5 s	[1] 2 416, [7] 67
Ammonia (H_2, N_2)	FB	G	Fe	450	150	28 s 7,800 GHSV	[6] 61
Ammonia (H_2, N_2)	FB	G	Fe	450	225	33 s 10,000 GHSV	[6] 61
Ammonia oxidation	Flame	G	Pt gauze	900	8	0.0026 s	[6] 115
Aniline (nitrobenzene, H_2)	B	L	$FeCl_2$ in H_2O	95–100	1	8 h	[1] 3 289
Aniline (nitrobenzene, H_2)	FB	G	Cu on silica	250–300	1	0.5–100 s	[7] 82
Aspirin (salicylic acid, acetic anhydride)	B	L	None	90	1	>1 h	[7] 89
Benzene (toluene)	TU	G	None	740	38	48 s 815 GHSV	[6] 36, [9] 109
Benzene (toluene)	TU	G	None	650	35	128 s	[1] 4 183, [7] 98
Benzoic acid (toluene, air)	SCST	LG	None	125–175	9–13	0.2–2 h	[7] 101
Butadiene (butane)	FB	G	Cr_2O_3, Al_2O_3	750	1	0.1–1 s	[7] 118
Butadiene (1-butene)	FB	G	None	600	0.25	0.001 s 34,000 GHSV	[3] 572
Butadiene sulfone (butadiene, SO_2)	CST	L	*t*-Butyl catechol	34	12	0.2 LHSV	[1] 5 192
i-Butane (*n*-butane)	FB	L	$AlCl_3$ on bauxite	40–120	18–36	0.5–1 LHSV	[4] 239, [7] 683
i-Butane (*n*-butane)	FB	L	Ni	370–500	20–50	1–6 WHSV	[4] 239
Butanols (propylene hydroformylation)	FB	L	PH_3-modified Co carbonyls	150–200	1,000	100 g L·h	[1] 5 373
Butanols (propylene hydroformylation)	FB	L	Fe pentacarbonyl	110	10	1 h	[7] 125
Calcium stearate	B	L	None	180	5	1–2 h	[7] 135
Caprolactam (cyclohexane oxime)	CST	L	Polyphosphoric acid	80–110	1	0.25–2 h	[1] 6 73, [7] 139
Carbon disulfide (methane, sulfur)	Furn.	G	None	500–700	1	1.0 s	[1] 6 322, [7] 144
Carbon monoxide oxidation (shift)	TU	G	Cu-Zn or Fe_2O_3	390–220	26	4.5 s 7,000 GHSV	[6] 44
Portland cement	Kiln	S		1,400–1,700	1	10 h	[11]
Chloral (Cl_2, acetaldehyde)	CST	LG	None	20–90	1	140 h	[7] 158
Chlorobenzenes (benzene, Cl_2)	SCST	LG	Fe	40	1	24 h	[1] 8 122
Coking, delayed (heater)	TU	LG	None	490–500	15–4	250 s	[1] 10 8
Coking, delayed (drum, 100 ft max height)	B	LG	None	500–440	4	0.3–0.5 ft/s vapor	[1] 10 8
Cracking, fluid catalytic	Riser	G	Zeolite	520–540	2–3	2–4 s	(14) 353
Cracking, hydro (gas oils)	FB	LG	Ni, SiO_2, Al_2O_3	350–420	100–150	1–2 LHSV	[11]
Cracking (visbreaking residual oils)	TU	LG	None	470–495	10–30	450 s, 8 LHSV	[11]
Cumene (benzene, propylene)	FB	G	H_3PO_4	260	35	23 LHSV	[11]
Cumene hydroperoxide (cumene, air)	CST	L	Metal porphyrins	95–120	2–15	1–3 h	[7] 191
Cyclohexane (benzene, H_2)	FB	G	Ni on Al_2O_3	150–250	25–55	0.75–2 LHSV	[7] 201
Cyclohexanol (cyclohexane, air)	SCST	LG	None	185–200	48	2–10 min	[7] 203
Cyclohexanone (cyclohexanol)	CST	L	N.A.	107	1	0.75 h	[8] (1963)
Cyclohexanone (cyclohexanol)	MT	G	Cu on pumice	250–350	1	4–12 s	[8] (1963)
Cyclopentadiene (dicyclopentadiene)	TJ	G	None	220–300	1–2	0.1–0.5 LHSV	[7] 212
DDT (chloral, chlorobenzene)	B	L	Oleum	0–15	1	8 h	[7] 233
Dextrose (starch)	CST	L	H_2SO_4	165	1	20 min	[8] (1951)
Dextrose (starch)	CST	L	Enzyme	60	1	100 min	[7] 217
Dibutylphthalate (phthalic anhydride, butanol)	B	L	H_2SO_4	150–200	1	1–3 h	[7] 227
Diethylketone (ethylene, CO)	TO	L	Co oleate	150–300	200–500	0.1–10 h	[7] 243
Dimethylsulfide (methanol, CS_2)	FB	G	Al_2O_3	375–535	5	150 GHSV	[7] 266
Diphenyl (benzene)	MT	G	None	730	2	0.6 s 3.3 LHSV	[7] 275, [8] (1938)
Dodecylbenzene (benzene, propylene tetramer)	CST	L	$AlCl_3$	15–20	1	1–30 min	[7] 283
Ethanol (ethylene, H_2O)	FB	G	H_3PO_4	300	82	1,800 GHSV	[2] 356, [7] 297
Ethyl acetate (ethanol, acetic acid)	TU, CST	L	H_2SO_4	100	1	0.5–0.8 LHSV	[10] 45, 52, 58
Ethyl chloride (ethylene, HCl)	TO	G	$ZnCl_2$	150–250	6–20	2 s	[7] 305
Ethylene (ethane)	TU	G	None	860	2	1.03 s 1,880 GHSV	[3] 411, [6] 13
Ethylene (naphtha)	TU	G	None	550–750	2–7	0.5–3 s	[7] 254
Ethylene, propylene chlorohydrins (Cl_2, H_2O)	CST	LG	None	30–40	3–10	0.5–5 min	[7] 310, 580
Ethylene glycol (ethylene oxide, H_2O)	TO	LG	1% H_2SO_4	50–70	1	30 min	[2] 398
Ethylene glycol (ethylene oxide, H_2O)	TO	LG	None	195	13	1 h	[2] 398
Ethylene oxide (ethylene, air)	FL	G	Ag	270–290	1	1 s	[2] 409, [7] 322
Ethyl ether (ethanol)	FB	G	WO_3	120–375	2–100	30 min	[7] 326
Fatty alcohols (coconut oil)	B	L	Na, solvent	142	1	2 h	[8] (1953)

TABLE 23-1 Residence Times and/or Space Velocities in Industrial Chemical Reactors (*Concluded*)

Product (raw materials)	Type	Reactor phase	Catalyst	*T*, °C	*P*, atm	Residence time or space velocity	Source and page†
Formaldehyde (methanol, air)	FB	G	Ag gauze	450–600	1	0.01 s	[2] 423
Glycerol (allyl alcohol, H_2O_2)	CST	L	H_2WO_4	40–60	1	3 h	[7] 347
Hydrogen (methane, steam)	MT	G	Ni	790	13	5.4 s 3,000 GHSV	[6] 133
Hydrodesulfurization of naphtha	TO	LG	Co-MO	315–500	20–70	1.5–8 LHSV 125 WHSV	[4] 285, [6] 179, [9] 201
Hydrogenation of cottonseed oil	SCST	LG	Ni	130	5	6 h	[6] 161
Isoprene (*i*-butene, formaldehyde)	FB	G	HCl, silica gel	250–350	1	1 h	[7] 389
Maleic anhydride (butenes, air)	FL	G	V_2O_5	300–450	2–10	0.1–5 s	[7] 406
Melamine (urea)	B	L	None	340–400	40–150	5–60 min	[7] 410
Methanol (CO, H_2)	FB	G	ZnO, Cr_2O_3	350–400	340	5,000 GHSV	[7] 421
Methanol (CO, H_2)	FB	G	ZnO, Cr_2O_3	350–400	254	28,000 GHSV	[3] 562
o-Methyl benzoic acid (xylene, air)	CST	L	None	160	14	0.32 h 3.1 LHSV	[3] 732
Methyl chloride (methanol, Cl_2)	FB	G	Al_2O_3 gel	340–350	1	275 GHSV	[2] 533
Methyl ethyl ketone (2-butanol)	FB	G	ZnO	425–475	2–4	0.5–10 min	[7] 437
Methyl ethyl ketone (2-butanol)	FB	G	Brass spheres	450	5	2.1 s 13 LHSV	[10] 284
Nitrobenzene (benzene, HNO_3)	CST	L	H_2SO_4	45–95	1	3–40 min	[7] 468
Nitromethane (methane, HNO_3)	TO	G	None	450–700	5–40	0.07–0.35 s	[7] 474
Nylon-6 (caprolactam)	TU	L	Na	260	1	12 h	[7] 480
Phenol (cumene hydroperoxide)	CST	L	SO_2	45–65	2–3	15 min	[7] 520
Phenol (chlorobenzene, steam)	FB	G	Cu, Ca phosphate	430–450	1–2	2 WHSV	[7] 522
Phosgene (CO, Cl_2)	MT	G	Activated carbon	50	5–10	16 s 900 GHSV	[11]
Phthalic anhydride (*o*-xylene, air)	MT	G	V_2O_5	350	1	1.5 s	[3] 482, 539, [7] 529
Phthalic anhydride (naphthalene, air)	FL	G	V_2O_5	350	1	5 s	[9] 136, [10] 335
Polycarbonate resin (bisphenol-A, phosgene)	B	L	Benzyltriethylammonium chloride	30–40	1	0.25–4 h	[7] 452
Polyethylene	TU	L	Organic peroxides	180–200	1,000–1,700	0.5–50 min	[7] 547
Polyethylene	TU	L	Cr_2O_3, Al_2O_3, SiO_2	70–200	20–50	0.1–1,000 s	[7] 549
Polypropylene	TO	L	R_2AlCl, $TiCl_4$	15–65	10–20	15–100 min	[7] 559
Polyvinyl chloride	B	L	Organic peroxides	60	10	5.3–10 h	[6] 139
i-Propanol (propylene, H_2O)	TO	L	H_2SO_4	70–110	2–14	0.5–4 h	[7] 393
Propionitrile (propylene, NH_3)	TU	G	CoO	350–425	70–200	0.3–2 LHSV	[7] 578
Reforming of naphtha (H_2/hydrocarbon = 6)	FB	G	Pt	490	30–35	3 LHSV 8,000 GHSV	[6] 99
Starch (corn, H_2O)	B	L	SO_2	25–60	1	18–72 h	[7] 607
Styrene (ethylbenzene)	MT	G	Metal oxides	600–650	1	0.2 s 7,500 GHSV	[5] 424
Sulfur dioxide oxidation	FB	G	V_2O_5	475	1	2.4 s 700 GHSV	[6] 86
t-Butyl methacrylate (methacrylic acid, *i*-butene)	CST	L	H_2SO_4	25	3	0.3 LHSV	[1] 5 328
Thiophene (butane, S)	TU	G	None	600–700	1	0.01–1 s	[7] 652
Toluene diisocyanate (toluene diamine, phosgene)	B	LG	None	200–210	1	7 h	[7] 657
Toluene diamine (dinitrotoluene, H_2)	B	LG	Pd	80	6	10 h	[7] 656
Tricresyl phosphate (cresyl, $POCl_3$)	TO	L	$MgCl_2$	150–300	1	0.5–2.5 h	[2] 850, [7] 673
Vinyl chloride (ethylene, Cl_2)	FL	G	None	450–550	2–10	0.5–5 s	[7] 699
Aldehydes (diisobutene, CO)	CST	LG	Co Carbonyl	150	200	1.7 h	(12) 173
Allyl alcohol (propylene oxide)	FB	G	Li phosphate	250	1	1.0 LHSV	(15) 23
Automobile exhaust	FB	G	Pt-Pd: 1–2 g/unit	400–600+	1		
Gasoline (methanol)	FB	G	Zeolite	400	20	2 WHSV	(13)*3* 383
Hydrogen cyanide (NH_3, CH_4)	FB	G	Pt-Rh	1150	1	0.005 s	(15) 211
Isoprene, polymer	B	L	$Al(i\text{-}Bu)_3$-$TiCl_4$	20–50	1–5	1.5–4 h	(15) 82
NO_x pollutant (with NH_3)	FB	G	V_2O_5-TiO_2	300–400	1–10		(14) 332
Vinyl acetate (ethylene + CO)	TO	LG	Cu-Pd	130	30	1 h L, 10 s G	(12) 140

*Abbreviations: reactors: batch (B), continuous stirred tank (CST), fixed bed of catalyst (FB), fluidized bed of catalyst (FL), furnace (Furn.), multitubular (MT), semicontinuous stirred tank (SCST), tower (TO), tubular (TU). Phases: liquid (L), gas (G), both (LG). Space velocities (hourly): gas (GHSV), liquid (LHSV), weight (WHSV). Not available, NA. To convert atm to kPa, multiply by 101.3.

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When the density is constant, replace $n_a/V_r = C_a$. How the constants α, β, γ, and δ are found from experimental conversion data is explained in Sec. 7.

BASIC REACTOR ELEMENTS

Reactions are carried out as batches or with continuous streams through a vessel. Flow reactors are distinguished by the degree of mixing of successive inputs. The limiting cases are: (1) with complete mixing, called an *ideal continuous stirred tank reactor* (CSTR), and (2) with no axial mixing, called a *plug flow reactor* (PFR).

Real reactors deviate more or less from these ideal behaviors. Deviations may be detected with *residence time distributions* (RTD) obtained with the aid of tracer tests. In other cases a mechanism may be postulated and its parameters checked against test data. The commonest models are combinations of CSTRs and PFRs in series and/or parallel. Thus, a stirred tank may be assumed completely mixed in the vicinity of the impeller and in plug flow near the outlet.

The combination of reactor elements is facilitated by the concept of *transfer functions.* By this means the Laplace transform can be found for the overall model, and the residence time distribution can be found after inversion. Finally, the chemical conversion in the model can be developed with the *segregation* and *maximum mixed* models.

Simple combinations of reactor elements can be solved directly. Figure 23-8, for instance, shows two CSTRs in series and with recycle through a PFR. The material balances with an n-order reaction $r = kC^n$ are

$$\frac{C_3}{C_2} = \frac{1}{1 + \dfrac{kV_rC_2}{RV'}}$$

$$V'C_f + RC_3 = (V' + R)C_1 + kV_{r1}C_1^n$$

$$(V' + R)C_1 = (V' + R)C_2 + kV_{r2}C_2^n \qquad (23\text{-}2)$$

Elimination of C_1 and C_3 from these equations will result in the desired relation between inlet C_f and outlet C_2 concentrations, although not in an explicit form except for zero or first-order reactions. Alternatively, the Laplace transform could be found, inverted and used to evaluate segregated or max mixed conversions that are defined later. Inversion of a transform like that of Fig. 23-8 is facilitated after replacing the exponential by some ratio of polynomials, a Padé approximation, as explained in books on linear control theory. Numerical inversion is always possible.

A stirred tank sometimes can be modeled as having a fraction α in bypass and a fraction β of the reactor volume stagnant. The material balance then is made up of

$$C = \alpha C_0 + (1 - \alpha)C_1 \qquad (23\text{-}3)$$

$$(1 - \alpha)V'C_0 = (1 - \alpha)V'C_1 + (1 - \beta)\,kV_rC_1^n \qquad (23\text{-}4)$$

where C_1 is the concentration leaving the active zone of the tank. Elimination of C_1 will relate the input and overall output concentrations. For a first-order reaction,

$$\frac{C_0}{C} = 1 + \frac{kV_r(1 - \beta)}{V'(1 - \alpha)} \qquad (23\text{-}5)$$

The two parameters α and β may be expected to depend on the amount of agitation.

A flow reactor with some deviation from plug flow, a quasi-PFR, may be modeled as a CSTR battery with a characteristic number n of stages, or as a dispersion model with a characteristic value of the dispersion coefficient or Peclet number. These models are described later.

MATERIAL BALANCES

Material and energy balances of common types of reactors are summarized in several tables of Sec. 7. For review purposes some material balances are restated here. For the nth stage of a CSTR battery,

$$V'_{n-1}C_{n-1} = V'_nC_n + V_rr_n \qquad (23\text{-}6)$$

or at constant density and a power law rate,

$$C_{n-1} = C_n + k\bar{t}_nC_n^\alpha \qquad (23\text{-}7)$$

The concentrations of all stages are found in succession when C_0 is known. For a PFR,

$$-V'\,dn_a = r_a\,dV_r = k\left(\frac{n_a}{V'}\right)^\alpha dV_r$$

$$kV_r = \int_{n_a}^{n_{a0}} V'\left(\frac{V'}{n_a}\right)^\alpha dn_a \qquad (23\text{-}8)$$

For operation with an inert tracer, the material balances are conveniently handled as Laplace transforms. For a stirred tank, the differential equation

$$C_0 = C + \bar{t}\,\frac{dC}{dt}, \qquad C = 0 \quad \text{when} \quad t = 0 \qquad (23\text{-}9)$$

becomes

$$\frac{\overline{C}}{\overline{C}_0} = \frac{1}{1 + \bar{t}s} \qquad (23\text{-}10)$$

and the partial differential equation of a plug flow vessel becomes

$$\frac{\overline{C}}{\overline{C}_0} = \exp(-\bar{t}s) \qquad (23\text{-}11)$$

The terms on the right are the transfer functions.

With the two units in series,

$$\frac{\overline{C}_2}{\overline{C}_0} = \left(\frac{\overline{C}_2}{\overline{C}_1}\right)\left(\frac{\overline{C}_1}{\overline{C}_0}\right) = \frac{\exp(-\bar{t}_2s)}{1 + \bar{t}_1s} \qquad (23\text{-}12)$$

and in parallel with a fraction β going to the mixed unit

$$\frac{\overline{C}}{\overline{C}_0} = \frac{\beta}{1 + \bar{t}_1s} + (1 - \beta)\exp(-\bar{t}_2s) \qquad (23\text{-}13)$$

where $\bar{t}_1 = \dfrac{V_{r1}}{\beta V'}$, $\bar{t}_2 = \dfrac{V_{r2}}{(1 - \beta)V'}$

HEAT TRANSFER AND MASS TRANSFER

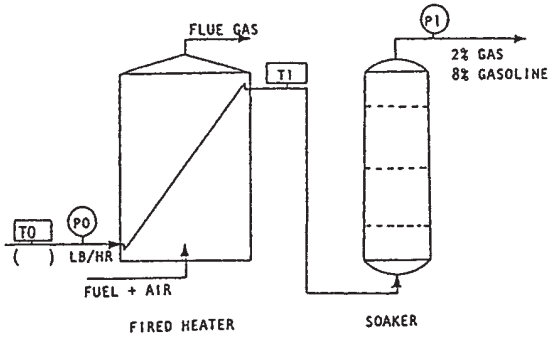
Temperature affects rates of reaction, degradation of catalysts, and equilibrium conversion. Some of the modes of heat transfer applied in reactors are indicated in Figs. 23-1 and 23-2. Profiles of some temperatures and compostions in reactors are in Figs. 23-3 to 23-6, 23-22, and 23-40. Many reactors with fixed beds of catalyst pellets have divided beds, with heat transfer between the individual sections. Such units can take advantage of initial high rates at high temperatures and higher equilibrium conversions at lower temperatures. Data for two such cases are shown in Table 23-2. For SO_2 the conversion attained in the fourth bed is 97.5 percent, compared with an adiabatic single bed value of 74.8 percent. With the three-bed ammonia reactor, final ammonia concentration is 18.0 percent, compared with the one-stage adiabatic value of 15.4 percent. Some catalysts deteriorate at much above 500°C, another reason for limiting temperatures.

Since reactors come in a variety of configurations, use a variety of operating modes, and may handle mixed phases, the design of provisions for temperature control draws on a large body of heat transfer theory and data. These extensive topics are treated in other sections of this Handbook and in other references. Some of the high points pertinent to reactors are covered by Rase (*Chemical Reactor Design for Process Plants,* Wiley, 1977). Two encyclopedic references are *Heat Exchanger Design Handbook* (5 vols., Hemisphere, 1983–date), and Cheremisinoff, ed. (*Handbook of Heat and Mass Transfer,* 4 vols., Gulf, 1986–1990), which has several articles addressed specifically to reactors.

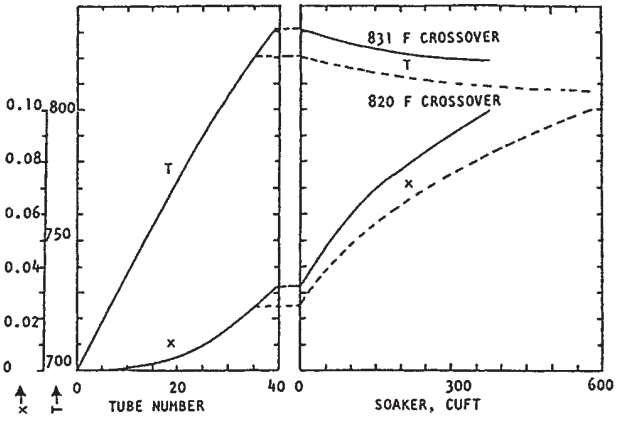
References to mass transfer are made throughout this section wherever multiple phases are discussed.

CASE STUDIES

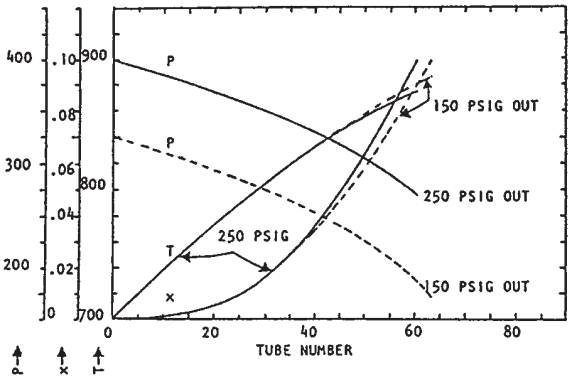
Exploration for an acceptable or optimum design of a new reaction process may need to consider reactor types, several catalysts, specifications of feed and product, operating conditions, and economic evaluations. Modifications to an existing process likewise may need to consider many cases. These efforts can be eased by commercial kinetics services. A typical one can handle up to 20 reactions in CSTRs or



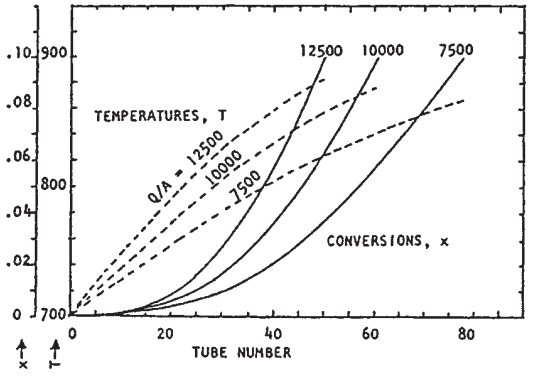
(a)



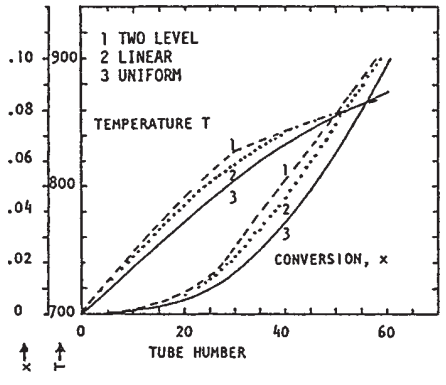
(b)



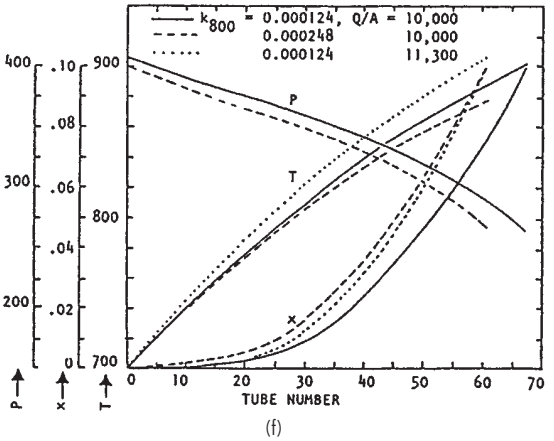
(c)



(d)



(e)



(f)

FIG. 23-4 (*a*) Visbreaking flowsketch, feed 160,000 lbm/h, $k_{800} = 0.000248$/s, tubes 5.05 in ID by 40 ft; (*b*) $Q/A = 10{,}000$ Btu/(ft²·h), $P_{out} = 250$ psig; (*c*) $Q/A = 10{,}000$ Btu/(ft²·h), $P_{out} = 150$ or 250 psig; (*d*) three different heat fluxes, $P_{out} = 250$ psig; (*e*) variation of heat flux, average 10,000 Btu/(ft²·h), $P_{out} = 250$ psig; (*f*) halving the specific rate. *T* in °F. To convert psi to kPa, multiply by 6.895; ft to m, multiply by 0.3048; in to cm, multiply by 2.54.

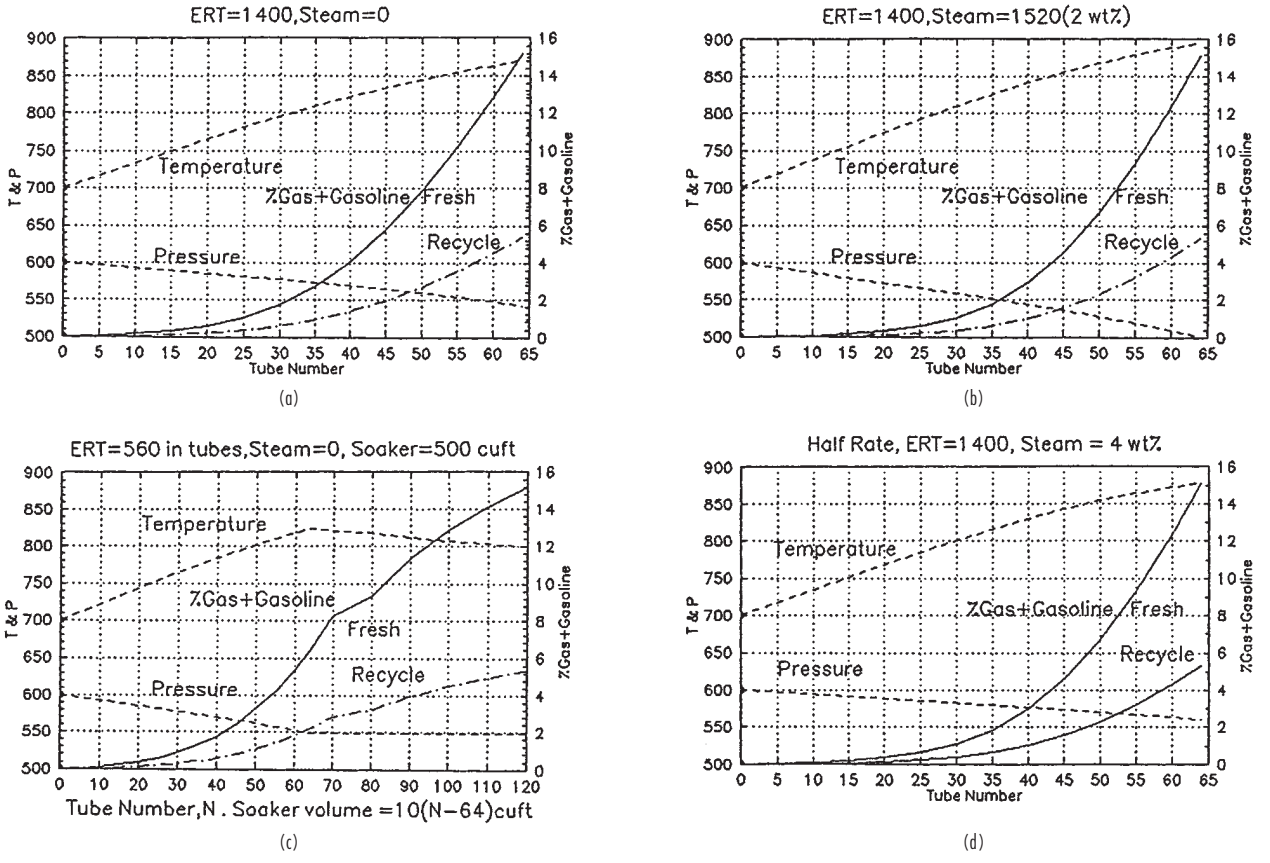


FIG. 23-5 Visbreaking fresh oil at 38,000 lbm/h, $k_{800} = 0.00012$/s, plus heavy gas oil at 38,000 lbm/h, $k_{800} = 0.00004$/s, 2% steam to put flow in the turbulent range. Tubes 4.25 in ID by 69 ft. (*a*) Heat flux 2,300 without steam. (*b*) Heat flux 2,600 with steam. (*c*) Soaker operation cuts the peak temperature by 50 ft and the heat flux by 30%. (*d*) When the feed rate turndown is 50%, steam rate is increased to 4% to keep flow turbulent. To convert ft to m, multiply by 0.3048; in to cm, multiply by 2.54; lb to kg/h, multiply by 0.454; Δt°F to Δt°C, multiply by 0.556.

PFRs, under isothermal, adiabatic, or heat transfer conditions in one or two phases. Outputs can provide profiles of composition, pressure, and temperature as well as vessel size.

When the kinetics are unknown, still-useful information can be obtained by finding equilibrium compositions at fixed temperature or adiabatically, or at some specified approach to the adiabatic temperature, say within 25°C (45°F) of it. Such calculations require only an input of the components of the feed and products and their thermodynamic properties, not their stoichiometric relations, and are based on Gibbs energy minimization. Computer programs appear, for instance, in Smith and Missen (*Chemical Reaction Equilibrium Analysis Theory and Algorithms,* Wiley, 1982), but the problem often is laborious enough to warrant use of one of the several available commercial services and their data banks. Several simpler cases with specified stoichiometries are solved by Walas (*Phase Equilibria in Chemical Engineering,* Butterworths, 1985).

For some widely practiced processes, especially in the petroleum industry, reliable and convenient computerized models are available from a number of vendors or, by license, from proprietary sources. Included are reactor-regenerator of fluid catalytic cracking, hydrotreating, hydrocracking, alkylation with HF or H_2SO_4, reforming with Pt or Pt-Re catalysts, tubular steam cracking of hydrocarbon fractions, noncatalytic pyrolysis to ethylene, ammonia synthesis, and other processes by suppliers of catalysts. Vendors of some process simulations are listed in the *CEP Software Directory* (AIChE, 1994).

Several excellent case studies that appear in the literature are listed, following.

Rase (*Case Studies and Design Data,* vol. 2 of *Chemical Reactor Design for Process Plants,* Wiley, 1977) has these items:

Styrene polymerization
Cracking of ethane to ethylene
Quench cooling in the ethylene process
Toluene dealkylation
Shift conversion
Ammonia synthesis
Sulfur dioxide oxidation
Catalytic reforming
Ammonia oxidation
Phthalic anhydride production
Steam reforming
Vinyl chloride polymerization
Batch hydrogenation of cottonseed oil
Hydrodesulfurization

Rase (*Fixed Bed Reactor Design and Diagnostics,* Butterworths, 1990) has a general computer program for reactor design and these case studies:

Methane-steam reaction
Hydrogenation of benzene to cyclohexane
Dehydrogenation of ethylbenzene to styrene

Tarhan (*Catalytic Reactor Design,* McGraw-Hill, 1983) has computer programs and results for these cases:

Toluene hydrodealkylation to benzene and methane
Phthalic anhydride by air oxidation of naphthalene
Trickle bed reactor for hydrodesulfurization

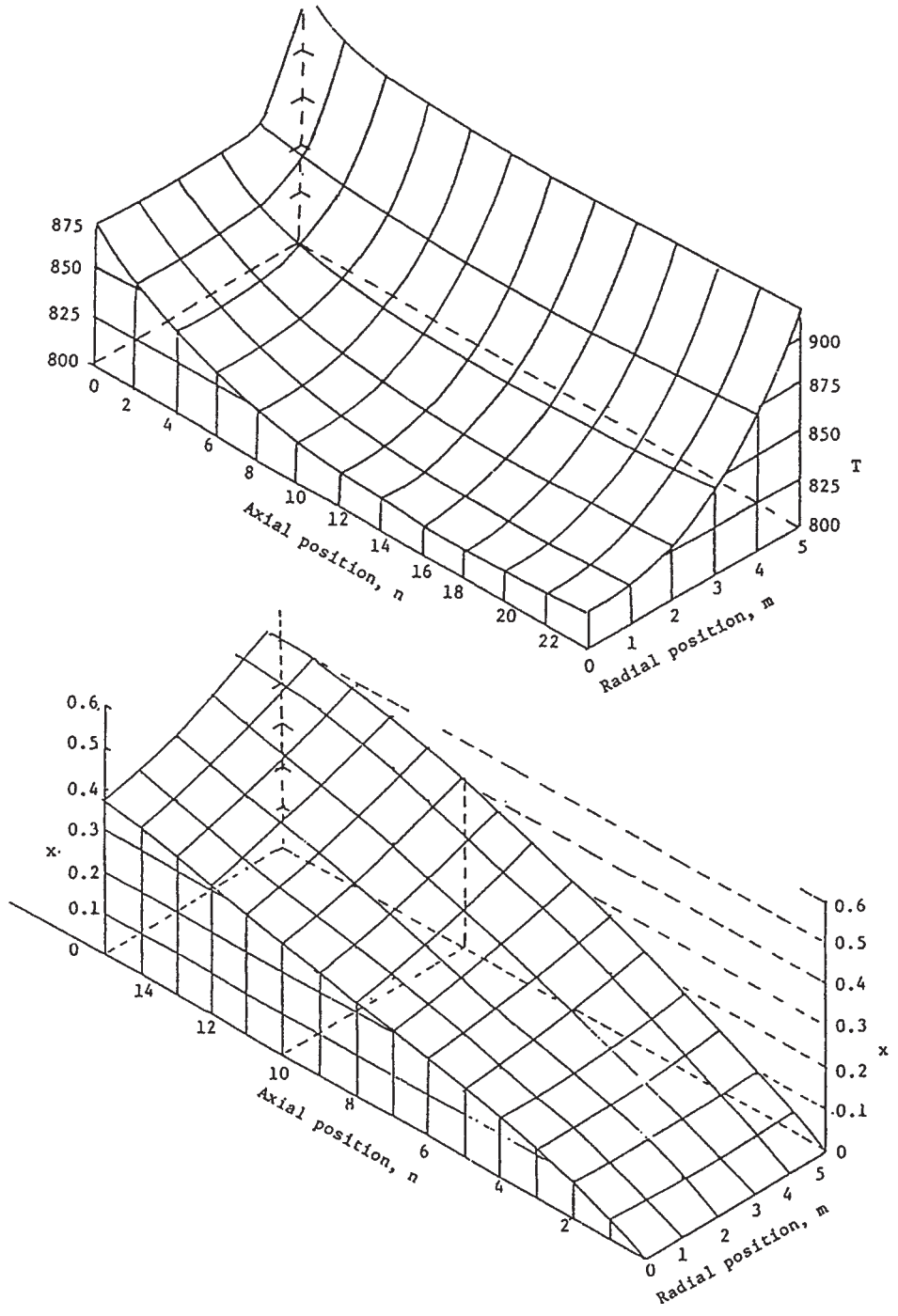


FIG. 23-6 Temperature in K and composition profiles in the styrene reactor. (*a*) Temperature profiles with $T' = 1000$, $T_{5.0} = 936.5$, and $hU/k_E = 0.5$. (*b*) Composition profiles with $T' = 1000$, $hU/k_E = 1000$. h = radial increment, U = heat-transfer coefficient at the wall, k_E = thermal conductivity, T in K. To convert K to R, multiply by 1.8.

T_0	T'	hU/k_E	$T_{5.0}$	n at 50% conversion
873	1000	0	873	—*
873	1000	0.5	936.5	25.3
873	1000	0.5	873	26.1
873	1000	1000	1000	15.6
873	1050	0.5	962.5	21.6
873	873	0.5	873	51.2

*The adiabatic reaction temperature reaches essentially the steady conditions, $x = 0.426$ and $T = 784$, after about 70 axial increments.

TABLE 23-2 Multibed Reactors, Adiabatic Temperature Rises and Approaches to Equilibrium*

Oxidation of SO_2 at atmospheric pressure in a four-bed reactor. Feed 6.26% SO_2, 8.3% O_2, 5.74% CO_2, and 79.7% N_2.

°C		Conversion, %	
In	Out	Plant	Equilibrium
463.9	592.8	68.7	74.8
455.0	495.0	91.8	93.4
458.9	465.0	96.0	96.1
435.0	437.2	97.5	97.7

Ammonia synthesis in a three bed reactor at 225 atm. Feed 22% N_2, 66% H_2, 12% inerts.

°C		Ammonia, %	
In	Out	Calculated	Equilibrium
399	518.9	13.0	15.4
427	488.9	16.0	19.0
427	470.0	18.0	21.7

*To convert atm to kPa multiply by 101.3.

SOURCE: Plant data and calculated design values from Rase, *Chemical Reactor Design for Process Plants,* Wiley, 1977.

Ramage, Graziani, Schipper, Krambeck, and Choi (*Advances in Chemical Engineering,* vol. 13, Academic Press, 1987, pp. 193–266):

Mobil's Kinetic Reforming Model

Dente and Ranzi (in Albright et al., eds., *Pyrolysis Theory and Industrial Practice,* Academic Press, 1983, pp. 133–175):

Mathematical modeling of hydrocarbon pyrolysis reactions

Shah and Sharma (in Carberry and Varma, eds., *Chemical Reaction and Reaction Engineering Handbook,* Dekker, 1987, pp. 713–721):

Hydroxylamine phosphate manufacture in a slurry reactor

Some aspects of a kinetic model of methanol synthesis are described in the first example, which is followed by a second example that describes coping with the multiplicity of reactants and reactions of some petroleum conversion processes. Then two somewhat simplified industrial examples are worked out in detail: mild thermal cracking and production of styrene. Even these calculations are impractical without a computer. The basic data and mathematics and some of the results are presented.

Example 1: Kinetics and Equilibria of Methanol Synthesis Although methanol from synthesis gas has been a large-scale industrial chemical for 70 years, the scientific basis of the manufacture apparently can stand some improvement, which was undertaken by Beenackers, Graaf, and Stamhuis (in Cheremisinoff, ed., *Handbook of Heat and Mass Transfer,* vol. 3, Gulf, 1989, pp. 671–699). The process occurs at 50 to 100 atm with catalyst of oxides of Cu-Zn-Al and a feed stream of H_2, CO, and CO_2. Three reactions were taken for the process:

$$CO + 3H_2 \Leftrightarrow CH_3OH$$

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad \text{(shift reaction)}$$

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH$$

In some earlier work the shift reaction was assumed always at equilibrium. Fugacities were calculated with the SRK and Peng-Robinson equations of state, and correlations were made of the equilibrium constants.

Various Langmuir-Hinshelwood mechanisms were assumed. CO and CO_2 were assumed to adsorb on one kind of active site, s1, and H_2 and H_2O on another kind, s2. The H_2 adsorbed with dissociation and all participants were assumed to be in adsorptive equilibrium. Some 48 possible controlling mechanisms were examined, each with 7 empirical constants. Variance analysis of the experimental data reduced the number to three possibilities. The rate equations of the three reactions are stated for the mechanisms finally adopted, with the constants correlated by the Arrhenius equation.

Kinetic studies were made with a spinning basket reactor using catalyst HaldorTopsoe MK 101, at three pressures and three temperatures.

Effectiveness factors of the porous catalyst were found by comparison with crushed particles 0.15 to 0.2 mm in diameter. For methanol formation the range of effectiveness was from approximately 0.9 at 490 K to 0.5 at 560 K, and for water formation 0.8 at 490 K and 0.5 at 560 K.

Simpler, mostly power law rate equations for the production of mixed alcohols from synthesis gas are cited by Forzatti, Tronconi, and Villa (in *Handbook of Heat & Mass Transfer,* vol. 4, Gulf, 1990, pp. 289–311). Agreements between their correlations and some data were deemed satisfactory. Rate equations are not necessarily the same on different catalysts.

Example 2: Coping with Multiple Reactants and Reactions

(*a*) Thermal cracking of ethane and propane is done to make primarily olefins but other products also are formed. A number of simplified reaction models are in use. One of these (Sundaram and Froment, *Chem. Eng. Sci.,* **32,** 601–617 [1977]; *Ind. Eng. Chem. Fund.,* **17,** 174–182 [1978]) takes these reactions to represent the cracking processes:

Ethane cracking

$$C_2H_6 \overset{k_1}{\rightleftharpoons} C_2H_4 + H_2$$

$$2C_2H_6 \xrightarrow{k_2} C_3H_8 + CH_4$$

$$C_3H_8 \xrightarrow{k_3} C_3H_6 + H_2$$

$$C_3H_8 \xrightarrow{k_4} C_2H_4 + CH_4$$

$$C_3H_6 \overset{k_5}{\rightleftharpoons} C_2H_2 + CH_4$$

$$C_2H_2 + C_2H_4 \xrightarrow{k_6} C_4H_6$$

Propane cracking

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2$$

$$C_3H_8 + C_2H_4 \longrightarrow C_2H_6 + C_3H_6$$

$$2C_3H_6 \longrightarrow 3C_2H_4$$

$$2C_3H_6 \longrightarrow 0.5C_6 + 3CH_4$$

$$C_3H_6 \rightleftharpoons C_2H_2 + CH_4$$

$$C_3H_6 + C_2H_6 \longrightarrow C_4H_8 + CH_4$$

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

$$C_2H_4 + C_2H_2 \longrightarrow C_4H_6$$

In the second paper the models were amplified: for ethane, 49 reactions with 11 molecular species and 9 free radicals; for propane, 80 reactions with 11 molecular species and 11 free radicals. The second paper has a list of 133 reactions involving light hydrocarbons and their first- or second-order specific rates.

(*b*) The feed to a typical fluidized catalytic cracking unit consists of liquid C_5 to C_{40} and contains thousands of individual species. This stream is made amenable to kinetic modeling by a process of lumping. A Mobil Corporation model (Weekman, "Lumps Models and Kinetics in Practice," *AIChE Monograph Series* No. 11, 1979) employs 10 lumps and 20 reactions. There are four lumps each in the boiling range, 222 to 342°C, of paraffins, naphthenes, aromatics, and aromatic substituents and also four above 342°C. The other two lumps are total C_1 to C_4 plus coke, and C_5 to 222°C. The specific rates are presumably proprietary data. In 1991, a seventh generation of this model was said to be in use.

(*c*) Commercial catalytic reformers upgrade naphthas in the C_5 to C_{12} range to high-octane gasoline with coproducts. Some 300 participants have been identified. In a Mobil Corporation model (Ramage et al., *Advances in Chemical Engineering,* vol. 13, Academic Press, 1987, pp. 193–266; Sapre, in Sapre and Krambeck, eds., *Chemical Reactions in Complex Mixtures,* Van Nostrand Reinhold, 1991, pp. 222–253) these have been lumped into pseudocomponents identified by carbon number and chemical nature. These lumps vary with the age of the catalyst. The table shows the 13 lumps adopted for the "start of the kinetic cycle."

Carbon number	Six-carbon-ring naphthenes, N_6	Five-carbon-ring naphthenes, N_5	Paraffins, P	Aromatics, A
C_{8+}	C_{8+} cyclohexanes (1)	C_{8+} cyclopentanes (2)	C_{8+} paraffins (3)	C_{8+} aromatics (4)
C_7	Methylcyclohexane (5)	Cyclopentanes (6)	Heptanes (7)	Toluene (8)
C_6	Cyclohexane (9)	Methylcyclopentane (10)	Hexanes (11)	Benzene (12)
C_{5-}				C_{5-} hydrocarbons (13)

The reaction network is shown in the paper. The kinetic characteristics of the lumps are proprietary. Originally, the model required 30 person-years of effort on paper and in the laboratory, and it is kept up to date.

Example 3: Thermal Cracking of Heavy Oils (Visbreaking) Mild thermal cracking is conducted in the tubes of a fired heater, sometimes fol-

lowed by an adiabatic holding drum. The cases to be studied are for making a product with reduced viscosity and with 8 percent gasoline plus 2 percent gas. A tube diameter is first selected with the rule that the cold oil velocity be 5 to 6 ft/s; this diameter is subject to change during the course of the calculation. For a specified heat flux, Q/A Btu/(h·ft^2 of tube surface), a number of parameters can be explored:

- Number of tubes of a given length, with and without a soaking drum
- Profiles of T, P, and fractional conversion x

A key consideration is that coking becomes likely in the vicinity of 900°F.

For the process of the flowsketch two different cases will be examined:

(*a*) Oil feed 160,000 lbm/h, $k_{800} = 0.000248$/s, tubes 5.05 in ID, 40 ft long.

(*b*) 38,000 lbm/h of fresh oil, $k_{800} = 0.00012$/s, + 38,000 lbm/h heavy gas oil, $k_{800} = 0.00004$/s, + 1,520 lbm/h steam; 64 tubes in series, 4.25 in ID, each 69 ft long.

In view of the necessity to be able to design for charge stocks of varied and not-well-characterized properties, some approximations are made. The main properties and operating variables are listed. n is the increment number of the integration and x is the fraction decomposed to gas + gasoline.

1. The components are original oil M, lbm/h, 10°API; cracked oil, 30°API; steam S, lbm/h; gasoline product 114 mol wt; gas product 28 mol wt.
2. The gas produced is a fraction $y = 0.2$ of the gas + gasoline made.
3. The specific rate at temperature T_n is

$$k = k_{800} \exp\left[50{,}000\left(\frac{1}{1{,}260} - \frac{1}{T_n + 460}\right)\right]$$

4. The mean density is figured on the assumption that the gas and gasoline are in the vapor phase and the cracked oil is in the liquid phase:

$$\rho_n = f(T_n, P_n, x_n) \tag{A}$$

5. The viscosity is that of the 30°API stock. $\nu_n = f(T_n)$, cSt.
6. Heat of reaction $\Delta H_r = 332$ Btu/(lbm gas + gasoline)
7. $Q_t A_t/M$ = heat input per increment of reactor, Btu/(h·lbm feed).
8. Each component of the feed has the enthalpy equation $H_i = A_i + B_i(T - 800)$.
9. The enthalpies of the mixtures leaving increments n and $n + 1$ of the reaction are expressed per unit mass of fresh oil,

$$H_n = f(T_n, x_n), \qquad H_{n+1} = f(T_{n+1}, x_{n+1})$$

10. The enthalpy balance over an increment of tubes is

$$H_n + \frac{Q_t A_t}{M} = H_{n+1} + \Delta H_r(x_{n+1} - x_n)$$

11. The temperature is derived from the enthalpy balance and is

$$T_{n+1} = T_0 + f(T_n, x_n, x_{n+1}) \tag{B}$$

where $T_0 = 800$ is the reference temperature for enthalpy.

12. The Reynolds number is

$$\mathrm{Re}_n = \frac{6.316\,(M + S)}{D\rho_n \nu_n}$$

D, in; ρ, lbm/ft^3; ν, cSt

13. The friction factor is given by Round's equation with a roughness factor $\varepsilon = 0.00015$ ft,

$$f_n = \frac{1.6434}{\ln(0.000243/D + 6.5/\mathrm{Re}_n)}$$

14. The pressure relation, lbm/in^2 is

$$P_{n+1} = P_n + \frac{3.356(10^{-6})L_t}{D^5}(M + S)^2\left(\frac{f_n}{\rho_n} + \frac{f_{n+1}}{\rho_{n+1}}\right) \tag{C}$$

The differential material balance of the first-order flow reaction is

$$Mdx = rdV_r = kCdV_r = \frac{kM(1-x)}{V'}dV_r = \frac{kM(1-x)}{(M+S)/\rho}dV_r$$

$$= k\rho\left(\frac{M}{M+S}\right)(1-x)\,V_t\,dN$$

The integral is rearranged to

$$x_{n+1} = 1 - (1 - x_n)\exp\left[-\frac{V_t}{M+S}\int_N^{N+\Delta N} k\rho\,dN\right]$$

Integration is by successive approximation, using essentially Euler's method. For the first trial,

$$x_{n+1}^{(1)} = 1 - (1 - x_n)\exp\left(-\frac{3600V_t}{M+S}(k\rho)_n \Delta N\right) \tag{D}$$

and for subsequent trials,

$$x_{n+1}^{(i+1)} = 1 - (1 - x_n)\exp\left\{-\frac{1800V_t}{M+S}\left[(k\rho)_n + (k\rho)_{n+1}^{(i)}\right]\right\} \tag{E}$$

Here,

k_n is a function of T_n

ρ_n is a function of T_n, P_n and x_n

V_t is the volume of one tube

ΔN is the number of tubes per reactor increment

3,600 compensates for the fact that k_n is per s and $M + S$ is per h

Calculation procedure

(*a*) In the preheat zone of the reactor, before cracking is appreciable, usually below 800°F, the pressure drop is found adequately enough by taking average densities and Reynolds numbers over this zone. The conditions at the inlet to the reaction zone are designated x_0, T_0, and P_0.

(*b*) Evaluate k_n, H_n, ρ_n, and ν_n at the inlet, where $n = 0$.

(c) Apply Eq. (D) to find the first approximation $x_{n+1}^{(1)}$ at the end of the first reactor increment.

(*d*) Find the next approximation $x_{n+1}^{(2)}$ with Eq. (E).

(*e*) If the condition

$$\frac{|x_{n+1}^{(2)} - x_{n+1}^{(1)}|}{x_{n+1}^{(2)} + x_{n+1}^{(1)}} \overset{?}{\leq} 0.01$$

is not satisfied, repeat the process; otherwise, continue with the next increment until the specified conversion is attained or some other specification is met or violated.

Equivalent residence time (ERT) can be found after the temperature profile has been established:

$$\mathrm{ERT} = \frac{V_r}{V'\rho_0}\int_0^1 \left(\frac{k}{k_{800}}\right)\rho\,dz \tag{F}$$

where z is the fractional distance along the total tube length. Engineers in the industry have a feel for what value of ERT is desirable with particular stocks and their conversion. The number usually is in the range of 500 to 1,500.

Results The results of computer calculations are summarized for the two operations by Figs. 23-4 and 23-5. In the second design, the equations had to be modified to take account of two feeds with different specific rates.

Example 4: Styrene from Ethylbenzene The principal reaction in the dehydrogenation of ethylbenzene is to styrene and hydrogen,

$$C_6H_5C_2H_5 \Leftrightarrow C_6H_5C_2H_3 + H_2$$

For a catalyst packed reactor, a rate equation was found by Wenner and Dybdal (*Chem. Eng. Prog.*, **44,** 275–286 [1948]):

$$R_c = k_r\left(P_E - \frac{(P_S P_H)^2}{K_e}\right) \text{ kg mol/(h·kg catalyst)} \tag{A}$$

$$k_r = \exp\left(9.44 - \frac{11{,}000}{T}\right) \tag{B}$$

$$K_e = \exp\left(15.69 - \frac{15{,}000}{T}\right) \tag{C}$$

where the pressures are in bar and temperatures in K.

The material balance with bulk flow in the axial direction z and diffusion in the radial direction r with diffusivity D gives rise to the equation

$$\frac{\partial(uC)}{\partial z} - \frac{D}{u}\left[\frac{\partial^2(uC)}{\partial r^2} + \frac{1}{r}\frac{\partial(uC)}{\partial r}\right] + \rho R_c = 0 \tag{D}$$

In terms of the fraction converted, the material balance becomes

$$\frac{\partial x}{\partial z} - \frac{D}{u}\left[\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right] - \frac{\rho}{u_0 C_0}R_c = 0 \tag{E}$$

Similarly, the heat balance gives rise to

$$\frac{\partial T}{\delta z} - \frac{k_e}{GC_p}\left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right] + \frac{\Delta H_r \rho}{GC_p}R_c = 0 \tag{F}$$

where G is the mass flow rate (2,500 kg/h as developed later).

Operating conditions The reactor is 10 cm ID, input of ethylbenzene is 0.069 kg mol/h, input of steam is 0.69 kgmol/h, total of 2,500 kg/h. Pressure is 1.2 bar, inlet temperature is 600°C. Heat is supplied at some constant temperature in a jacket. Performance is to be found with several values of heat transfer coefficient at the wall, including the adiabatic case.

Data

Bulk density of catalyst	$\rho = 1{,}440$ kg/m^3
Heat of reaction	$\Delta H_r = 140{,}000$ kJ/kg mol
Thermal conductivity	$k_e = 0.45$ W/m K
Ratio of diffusivity to linear velocity	$D/u = 0.000427$ m
Specific heat of the mixture	$C_p = 2.18$ kJ/kg K

In terms of the fractional conversion and the ideal gas law, the rate equation becomes

$$R_c = 1.2\exp\left(9.44 - \frac{11{,}000}{T}\right)\left[\frac{1-x}{11+x} - \frac{1.2}{K_e}\left(\frac{x}{11+x}\right)^2\right] \tag{G}$$

Substitution of the data transforms the heat and material balances into Eqs. (H) and (I):

$$\frac{\partial T}{\partial z} = a\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) - bR_c, \qquad a = 0.000297, \qquad b = 37{,}000 \tag{H}$$

$$\frac{\partial x}{\partial z} = c\left(\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right) + dR_c, \qquad c = 0.000427, \qquad d = 164 \tag{I}$$

At the center, Eqs. (H) and (I) become, after application of l'Hopital's rule,

$$\frac{\partial T}{\partial z} = 2a\frac{\partial^2 T}{\partial r^2} - bR_c \tag{J}$$

$$\frac{\partial x}{\partial r} = 2c\frac{\partial^2 T}{\partial r^2} + dR_c \tag{K}$$

At the wall,

$$-k_e\frac{\partial T}{\partial r} = U(T - T') \tag{L}$$

Eqs. (H) through (L) will be solved by the explicit finite difference method. Substitute

$$\frac{\partial T}{\partial z} = \frac{T_{m,n+1} - T_{m,n}}{k}, \qquad k = \Delta z \tag{M}$$

$$\frac{\partial T}{\partial r} = \frac{T_{m,n+1} - T_{m,n-1}}{2h}, \qquad h = \Delta r \tag{N}$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{m+1,n} - 2T_{m,n} + T_{m-1,n}}{h^2} \tag{O}$$

and similarly for variable x.

The substituted finite difference equations will contain the terms

$$M' = \frac{0.000427k}{h^2} = 0.250, \qquad \text{for stability} \tag{P}$$

$$M = \frac{0.000297k}{h^2} = 0.174$$

The choice $M' = 0.250$ is to prevent negative coefficients and thus an unstable iterative process.

The finite difference equations will be formulated with five radial increments $m = 0, 1, 2, 3, 4, 5$, and for as many axial increments as necessary to obtain 50 percent conversion. Accordingly,

$$h = \Delta r = 1 \text{ cm}$$

$$k = \Delta z = \frac{0.250}{0.000427} = 585 \text{ cm}$$

At the center, $m = 0$, the finite difference equations become

$$T_{0,n+1} = 4MT_{1,n} + (1 - 4M)T_{0,n} - kbR_{c0,n} \tag{Q}$$

$$x_{0,n+1} = 4M'x_{1,n} + (1 - 4M')x_{0,n} + kdR_{c0,n} \tag{R}$$

When $m = 1, 2, 3$, or 4,

$$T_{m,n+1} = M\left(1 + \frac{1}{2m}\right)T_{m+1,m} + (1 - 2M)\,T_{m,n} + M\left(1 - \frac{1}{2m}\right)T_{m-1,n} - kbR_{cm,n} \tag{S}$$

$$x_{m,n+1} = M\left(1 + \frac{1}{2m}\right)x_{m+1,n} + (1 - 2M)\,x_{m,n} + M\left(1 - \frac{1}{2m}\right)x_{m-1,n} + kdR_{cm,n} \tag{T}$$

At the wall, $m = 5$, the heat-transfer coefficient is U and the heating gas has temperature T_n',

$$T_{5,n} = \frac{T_{4,n} + (hU/k_e)T_n'}{1 + hU/k_e} \tag{U}$$

$$x_{5,n} = x_{4,n} \tag{V}$$

The rate equation becomes

$$R_{cm,n} = 1.2\,k_r\left[\frac{1 - x_{m,n}}{11 + x_{m,n}} - \frac{1.2}{K_e}\left(\frac{x_{m,n}}{11 + x_{m,n}}\right)^2\right] \tag{W}$$

$$k_r = \exp\left(9.44 - \frac{11{,}000}{T_{m,n}}\right) \tag{X}$$

$$K_e = \exp\left(15.69 - \frac{15{,}000}{T_{m,n}}\right) \tag{Y}$$

At this point the computer takes over. Cases with several values of jacket temperature and several values of heat-transfer coefficient, or hU/k_e, are examined, and also several assumptions about the temperature at the wall at the inlet. Eq. (U) with $n = 0$ could be used. The number of axial increments are found for several cases of 50% conversion. Two of the profiles of temperature or conversion are shown in Fig. 23-6.

The Crank-Nicholson implicit method and the method of lines for numerical solution of these equations do not restrict the radial and axial increments as Eq. (P) does. They are more involved procedures, but the burden is placed on the computer in all cases.

A version of this problem is solved by Jenson and Jeffreys (*Mathematical Methods in Chemical Engineering*, Academic Press, 1977).

More up-to-date data of this process are employed in a study by Rase (*Fixed Bed Reactor Design and Diagnostics*, Butterworths, 1990, pp. 275–286). In order to keep the pressure drop low, radial flow reactors are used, two units in series with reheating between them. Simultaneous formation of benzene, toluene, and minor products is taken into account. An economic comparison is made of two different catalysts under a variety of operating conditions. Some of the computer printouts are shown there.

RESIDENCE TIME DISTRIBUTION (RTD) AND REACTOR EFFICIENCY

The distribution of residence times of reactants or tracers in a flow vessel, the RTD, is a key datum for determining reactor performance, either the expected conversion or the range in which the conversion must fall. In this section it is shown how tracer tests may be used to establish how nearly a particular vessel approaches some standard ideal behavior, or what its efficiency is. The most useful comparisons are with complete mixing and with plug flow. A glossary of special terms is given in Table 23-3, and major relations of tracer response functions are shown in Table 23-4.

TRACERS

Nonreactive substances that can be used in small concentrations and that can easily be detected by analysis are the most useful tracers. When making a test, tracer is injected at the inlet of the vessel along with the normal charge of process or carrier fluid, according to some definite time sequence. The progress of both the inlet and outlet concentrations with time is noted. Those data are converted to a residence time distribution (RTD) that tells how much time each fraction of the charge spends in the vessel.

An RTD, however, does not represent the mixing behavior in a vessel uniquely, because several arrangements of the internals of a vessel may give the same tracer response, for example, any series arrangements of reactor elements such as plug flow or complete mixing. This is a consequence of the fact that tracer behavior is represented by linear differential equations. The lack of uniqueness limits direct application of tracer studies to first-order reactions with constant specific rates. For other reactions, the tracer curve may determine the upper and lower limits of reactor performance. When this range is not too broad, the result can be useful. Tracer data also may be taken at several representative positions in the vessel in order to develop a realistic model of the reactor.

REACTOR EFFICIENCY

One quantitative measure of reactor efficiency at a conversion level x is the ratio of the mean residence time or the reactor volume in a plug flow reactor to that of the reactor in question,

$$\eta_x = \left(\frac{\bar{t}_{pf}}{\bar{t}}\right)_x = (V_{pf}/V)_x \tag{23-14}$$

TABLE 23-3 Glossary of RTD Terms

Closed end vessel One in which the inlet and outlet streams are completely mixed and dispersion occurs only between the terminals. At the inlet where $z = 0$, $uC_0 = [uC - D_e(\partial C/\partial z)]_{z=0}$; at the outlet where $x = L$, $(\partial C/\partial z)_{z=L} = 0$. These are called *Danckwerts' boundary conditions.*

Concentration The main special kinds are: C_δ, that of the effluent from a vessel with impulse input of tracer; $C^0 = m/V_r$, the initial mean concentration resulting from impulse input of magnitude m; C_u, that of the effluent from a vessel with a step input of magnitude C_f.

Dispersion The movement of aggregates of molecules under the influence of a gradient of concentration, temperature, and so on. The effect is represented by Fick's law with a dispersion coefficient substituted for molecular diffusivity. Thus, rate of transfer $= -D_e(\partial C/\partial z)$.

Impulse An amount of tracer injected instantaneously into a vessel at time zero. The symbol $m\delta(t - a)$ represents an impulse of magnitude m injected at time $t = a$. The effluent concentration resulting from an impulse input is designated C_δ.

Maximum mixedness Exists when any molecule that enters a vessel immediately becomes associated with those molecules with which it will eventually leave the vessel; that is, with those molecules that have the same life expectation. A state of MM is associated with every RTD.

Mixing, ideal or complete A state of complete uniformity of composition and temperature in a vessel. In flow, the residence time varies exponentially, from zero to infinity.

Peclet number for dispersion $\mathrm{Pe} = uL/D_e$ where u is a linear velocity, L is a linear dimension, and D_e is the dispersion coefficient. In packed beds, $\mathrm{Pe} = ud_p/D_e$, where u is the interstitial velocity and d_p is the pellet diameter.

Plug flow A condition in which all effluent molecules have had the same residence time.

Residence time distribution (RTD) In the case of elutriation of tracer from a vessel that contained an initial average concentration C^0, the area under a plot of $E(t) = C_{\text{effluent}}/C^0$ between the ordinates at t_1 and t_2 is the fraction of the molecules that have residence times in this range. In the case of constant input of concentration C_f to a vessel with zero initial concentration, the ratio $F(t) = C_{\text{effluent}}/C_f$ at t_1 is the fraction of molecules with residence times less than t_1.

Residence time, mean The average time spent by the molecules in a vessel. Mathematically, it is the first moment of the effluent concentration from a vessel with impulse input, or

$$\bar{t} = \frac{\int_0^\infty tC_\delta\,dt}{\int_0^\infty C_\delta\,dt.}$$

Segregated flow Occurs when all molecules that enter together also leave together. A state of aggregation is associated with every RTD. Each aggregate of molecules reacts independently of every other aggregate; thus, as an individual batch reactor.

Skewness The third moment of a residence time distribution:

$$\gamma^3(t) = \int_0^\infty (t - \bar{t})^3 E(t)\,dt.$$

It is a measure of asymmetry.

Step An input in which the concentration of tracer is changed to some constant value C_f at time zero and maintained at this level indefinitely. The symbol $C_f u(t - a)$ represents a step of magnitude C_f beginning at $t = a$. The resulting effluent concentration is designated C_u.

Variance The second moment of the RTD. There are two forms: one in terms of the absolute time, designated $\sigma^2(t)$; and the other in terms of reduced time, $t_r = t/\bar{t}$, designated $\sigma^2(t_r)$.

$$\sigma^2(t) = \frac{\int_0^\infty (t - \bar{t})^2 C_\delta\,dt}{\int_0^\infty C_\delta\,dt} = \int_0^\infty (t - \bar{t})^2 E(t)\,dt$$

$$\sigma^2(t_r) = \frac{\sigma^2(t)}{\bar{t}^2} = \int_0^\infty (t_r - 1)^2 E(t_r)\,dt_r$$

TABLE 23-4 Tracer Response Functions

Mean residence time:

$$\bar{t} = \frac{\int_0^\infty tC_\delta\,dt}{\int_0^\infty C_\delta\,dt} = \frac{\int_0^{C_{u\infty}} t\,dC_u}{C_{u\infty}}$$

Initial mean concentration with impulse input,

$$C^0 = \frac{m}{V_r} = \left(\frac{V'}{V_r}\right)\int_0^\infty C_\delta\,dt = \frac{\int_0^\infty C_\delta\,dt}{\bar{t}}$$

Reduced time: $$t_r = \frac{t}{\bar{t}}$$

Residence time distribution:

$$E(t) = \frac{C_\delta}{\int_0^\infty C_\delta\,dt} = \frac{E(t_r)}{\bar{t}} = \frac{dF(t)}{dt}$$

Residence time distribution, normalized,

$$E(t_r) = \frac{\text{impulse output}}{\text{initial mean concentration}}$$

$$= \frac{C_\delta}{C^0} = \frac{\bar{t}C_\delta}{\int_0^\infty C_\delta\,dt} = \bar{t}\,E(t) = \frac{dF(t)}{dt}$$

Age: $$F(t) = \frac{\text{step output}}{\text{step input}}$$

$$= \frac{C_u}{C_f} = \frac{\int_0^t C_\delta\,dt}{\int_0^\infty C_\delta\,dt} = F(t_r)$$

Internal age: $$I(t) = 1 - F(t)$$

Intensity: $$\Lambda(t) = \frac{E(t)}{1 - F(t)} = \frac{E(t)}{I(t)}$$

Variance:

$$\sigma^2(t) = \int_0^\infty (t - \bar{t})^2 E(t)\,dt = -\bar{t}^2 + \frac{\int_0^\infty t^2 C_\delta\,dt}{\int_0^\infty C_\delta\,dt}$$

Variance, normalized:

$$\sigma^2(t_r) = \frac{\sigma^2(t)}{\bar{t}^2} = -1 + \frac{\int_0^\infty t^2 C_\delta\,dt}{\int_0^\infty C_\delta\,dt}$$

$$= \int_0^1 (t_r - 1)^2\,dF(t_r)$$

Skewness, third moment:

$$\gamma^3(t_r) = \int_0^\infty (t_r - 1)^3 E(t_r)\,dt_r$$

The conversion level sometimes is taken at 95 percent of equilibrium, but there is no universal standard.

Other measures of efficiency are derived from the experimental RTD, which is characterized at least approximately by the variance $\sigma^2(t_r)$. This quantity is zero for plug flow and unity for complete mixing, and thus affords natural bounds to an efficiency equated to the variance. It is possible, however, for the variance to fall out of the range (0,1) when stagnancy or bypassing occurs.

A related measure of efficiency is the equivalent number of stages n_{erlang} of a CSTR battery with the same variance as the measured RTD. Practically, in some cases 5 or 6 stages may be taken to approximate plug flow. The dispersion coefficient D_e also is a measure of deviation from plug flow and has the merit that some limited correlations in terms of operating conditions have been obtained.

No correlations of $\sigma^2(t_r)$ or n_{erlang} have been achieved in terms of operating variables. At present, the chief value of RTD studies is for the diagnosis of the performance of existing equipment; for instance, maldistribution of catalyst in a packed reactor, or bypassing or stagnancy in stirred tanks. Reactor models made up of series and/or parallel elements also can be handled theoretically by these methods.

TRACER RESPONSE

The unsteady material balances of tracer tests are represented by linear differential equations with constant coefficients that relate an input function $C_f(t)$ to a response function of the form

$$\sum_0^n a_n \frac{dC^n}{dt^n} = C_f \qquad (23\text{-}15)$$

The general form of the material balance is the familiar one,

Inputs + Sources = Outputs + Sinks + Accumulations

as described in the "Modeling Chemical Reactors" section. For the special case of initial equilibrium or dead state (all derivatives = 0 at time 0), the transformed function of the preceding equation is

$$\overline{C} = \frac{\overline{C}_f}{\Sigma\, a_n s^n} \tag{23-16}$$

and $C(t)$ is found by inversion with a table of Laplace transform pairs. The individual transform is defined as

$$\overline{C} = C(s) = \int_0^\infty \exp(-st) C(t)\, dt \tag{23-17}$$

The ratio of transforms,

$$G(s) = \frac{C(s)}{C_f(s)} \tag{23-18}$$

is called a *transfer function.* The concept is useful in the representation of systems consisting of several elements in series and parallel.

A particularly useful property of linear differential equations may be explained by comparing an equation and its derivative in operator form,

$$f(D)y = g(t) \qquad \text{and} \qquad f(D)z = \frac{dg(t)}{dt} \tag{23-19}$$

where the RHS of the second equation is the derivative of the RHS of the first. The property in question is that $z = dy/dt$. The chief use of this property in this area is with the step and impulse functions, the impulse being the derivative of the step. Often problems are easier to visualize and formulate in terms of the step input, but the desired solution may be for the impulse input which gives the RTD directly.

Kinds of Inputs Since a tracer material balance is represented by a linear differential equation, the response to any one kind of input is derivable from some other known input, either analytically or numerically. Although in practice some arbitrary variation of input concentration with time may be employed, five mathematically simple input signals supply most needs. *Impulse* and *step* are defined in the Glossary (Table 23-3). *Square pulse* is changed at time *a,* kept constant for an interval, then reduced to the original value. *Ramp* is changed at a constant rate for a period of interest. A *sinusoid* is a signal that varies sinusoidally with time. Sinusoidal concentrations are not easy to achieve, but such variations of flow rate and temperature are treated in the vast literature of automatic control and may have potential in tracer studies.

RESPONSE FUNCTIONS

The chief quantities based on tracer tests are summarized in Table 23-4. Effluent concentrations resulting from impulse and step inputs are designated C_δ and C_u, respectively. The initial mean concentration resulting from an impulse of magnitude m into a vessel of volume V_r is $C^0 = m/V_r$. The mean residence time is the ratio of the vessel volume to the volumetric flow rate, $\bar{t} = V_r/V'$ or $\bar{t} = \int_0^\infty tC_\delta\, dt / \int_0^\infty C_\delta\, dt$. The reduced time is $t_r = t/\bar{t}$.

Residence time distributions are used in two forms: Normalized, $E(t_r) = C_\delta/C^0$; or plain, $E(t) = C_\delta/\int_0^\infty C_\delta\, dt$. The relation between them is $E(t_r) = \bar{t}E(t)$. On time plots, the area under either RTD is unity: $\int_0^\infty E(t_r)\, dt_r = \int_0^\infty E(t)\, dt = 1$. Moreover, the area between the ordinates at t_1 and t_2 is the fraction of the total effluent that has spent the period between those times in the vessel.

The *age function* is defined in terms of the step input as

$$F(t) = \frac{C_u}{C_f} = \int_0^t E(t)\, dt$$

Relations to other functions are in Table 23-3.

The intensity function $\Lambda(t) = E(t)/[1 - F(t)]$ occurs in the maximum mixing concept and is of value, for instance, in detecting maldistributions of catalyst and channeling in a packed vessel.

The Erlang number n_{erlang} and the variances $\sigma^2(t_r)$ and $\sigma^2(t)$ are single parameter characterizations of RTD curves. The skewness $\gamma^3(t)$, and higher moments can be used to represent RTD curves more closely if the data are accurate enough.

ELEMENTARY MODELS

Real reactors may conform to some sort of ideal mixing patterns, or their performance may be simulated by combinations of ideal models. The commonest ideal models are the following:

- *Plug flow reactor* (*PFR*), in which all portions of the charge have the same residence time. The concentration varies with time and position, according to the equation,

$$\frac{\partial C}{\partial t} + V' \frac{\partial C}{\partial V_r} = 0$$

- *Continuous stirred tank reactor* (*CSTR*), with the effluent concentration the same as the uniform vessel concentration. With a mean residence time $\bar{t} = V_r/V'$, the material balance is

$$\bar{t}\, \frac{dC}{dt} + C = \text{Input concentration}$$

- *Dispersion model* is based on Fick's diffusion law with an empirical dispersion coefficient D_e substituted for the diffusion coefficient. The material balance is

$$\frac{\partial C}{\partial t} + V' \frac{\partial C}{\partial V_r} - D_e \frac{\partial^2 C}{\partial V_r^2} = 0$$

- *Laminar* or power law velocity distribution in which the linear velocity varies with radial position in a cylindrical vessel. Plug flow exists along any streamline and the mean concentration is found by integration over the cross section.
- *Distribution models* are curvefits of empirical RTDs. The Gaussian distribution is a one-parameter function based on the statistical rule with that name. The Erlang and gamma models are based on the concept of the multistage CSTR. RTD curves often can be well fitted by ratios of polynomials of the time.

Figure 23-7 illustrates the responses of CSTRs and PFRs to impulse or step inputs of tracers.

REAL BEHAVIOR

An empty tubular reactor often can be simulated as a PFR or by a dispersion model with a small value of the dispersion coefficient. Stirred tank performance often is nearly completely mixed (CSTR), or the model may be modified by taking account of bypass zones, stagnant zones, or other parameters associated with the geometry and operation of the vessel. The additional parameters contribute to the mathematical complexity of the model. Sometimes the vessel can be visualized as a zone of complete mixing in the vicinity of impellers followed by plug flow zones elsewhere; thus, CSTRs followed by PFRs. Packed beds usually deviate substantially from plug flow. The dispersion model and some combinations of PFRs and CSTRs or multiple CSTRs in series may approximate their behavior. Fluidized beds in small sizes approximate CSTR behavior, but large ones exhibit bypassing, stagnancy, nonhomogeneous regions, and several varieties of contact between particles and fluid.

The concept of transfer functions facilitates the combination of linear elements. The rule is:

Output transform = (Transfer function) (Input transform)

Figure 23-8 develops the overall transform of a process with a PFR in parallel with two CSTRs in series. $C(t)$ is found from $C(s)$ by inversion of the output transform.

TRACER EQUATIONS

Differential equations and their solutions will be stated for the elementary models with the main kinds of inputs. Since the ODEs are linear, solutions by Laplace transforms are feasible.

Ideal CSTR With a step input of magnitude C_f the unsteady material balance is

$$V_r \frac{dC}{dt} + V'C = V'C_f \tag{23-20}$$

whose integral is

$$\frac{C}{C_f} = F(t_r) = 1 - \exp(-t_r) \tag{23-21}$$

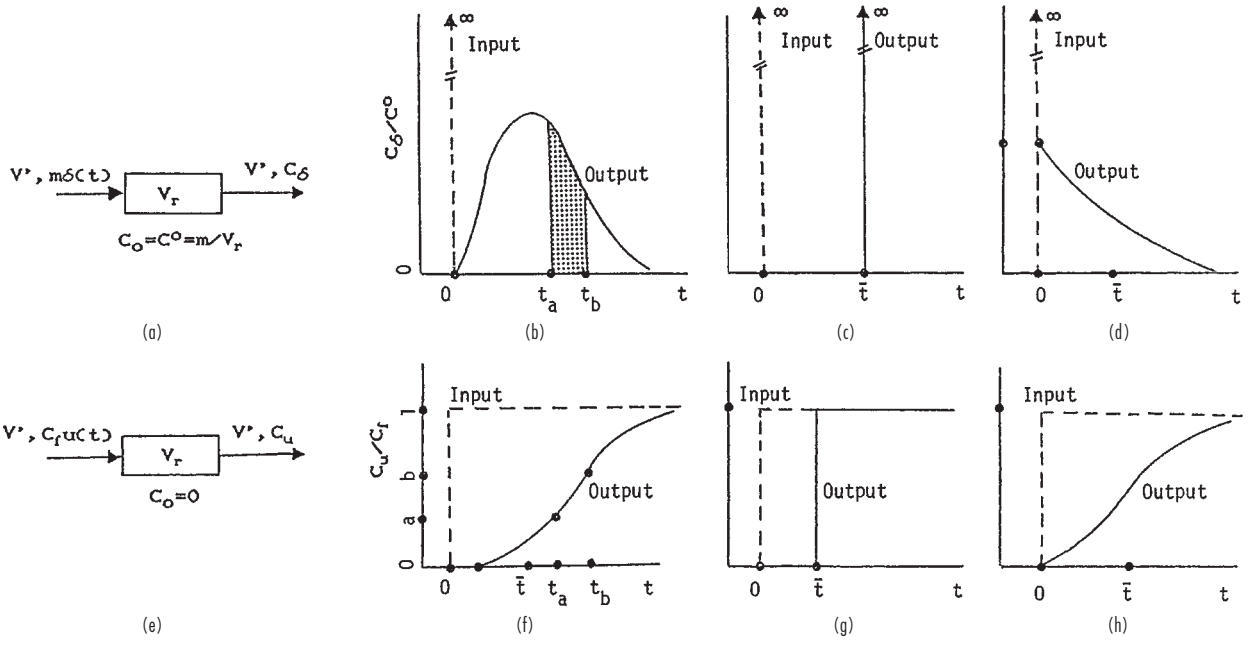


FIG. 23-7 Impulse and step inputs and responses. Typical, PFR and CSTR. (*a*) Experiment with impulse input of tracer. (*b*) Typical behavior; area between ordinates at t_a and t_b equals the fraction of the tracer with residence time in that range. (*c*) Plug flow behavior; all molecules have the same residence time. (*d*) Completely mixed vessel; residence times range between zero and infinity. (*e*) Experiment with step input of tracer; initial concentration zero. (*f*) Typical behavior; fraction with ages between t_a and t_b equals the difference between the ordinates, $b - a$. (*g*) Plug flow behavior; zero response until $t = \bar{t}$ has elapsed, then constant concentration C_f. (*h*) Completely mixed behavior; response begins at once, and ultimately reaches feed concentration.

With an impulse input of magnitude m or an initial mean concentration $C^0 = m/V_r$, the material balance is

$$\frac{dC}{dt_r} + C = 0 \qquad \text{when} \qquad C = C^0,\ t = 0 \tag{23-22}$$

and

$$\frac{C}{C^0} = E(t_r) = \exp(-t_r) \tag{23-23}$$

From these results it is clear that $E(t_r) = dF(t_r)/dt_r$.

Plug Flow Reactor (PFR) The material balance over a differential volume dV_r is

$$V'C = V'(C + dC) + dV_r \frac{\partial C}{\partial t}$$

or

$$\frac{\partial C}{\partial t} + V' \frac{\partial C}{V_r} = 0 \tag{23-24}$$

With step input the boundary conditions are

$$C(0,t) = C_f u(t) \qquad C(V_r,0) = 0 \tag{23-25}$$

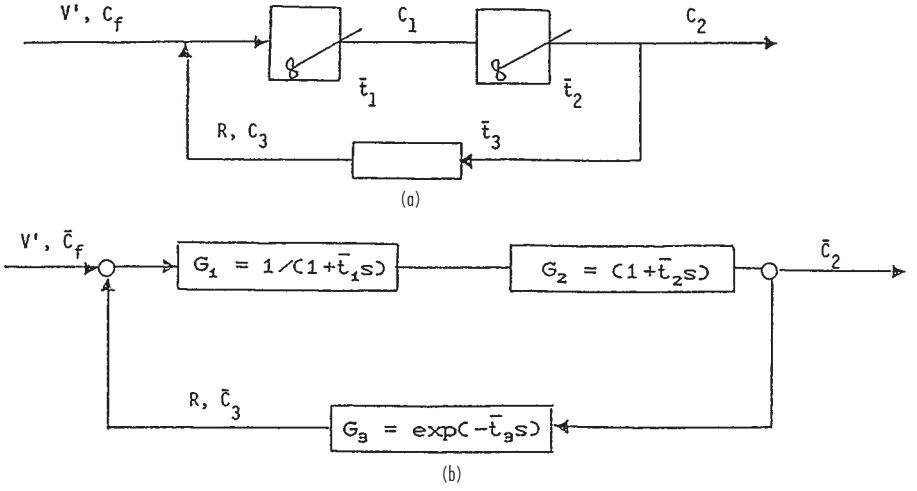


FIG. 23-8 Diagrams of a composite process: (*a*) process flow diagram, (*b*) transfer function diagram. The overall transfer function is:

$$\frac{\bar{C}_2}{\bar{C}_f} = \frac{1}{(1 + R/V')(1 + t_1 s)(1 + t_2 s) - (R/V')\exp(-t_3 s)}$$

By Laplace transform the solution is

$$\frac{C}{C_f} = F(t) = u(t-\bar{t}) = 0 \quad \text{when} \quad t \le \bar{t}$$
$$= 1 \quad \text{when} \quad t \ge \bar{t} \tag{23-26}$$

The response to impulse input is found by differentiation,

$$\frac{C}{C^0} = E(t_r) = \bar{t}\delta(t-\bar{t}) = \bar{t}\delta[\bar{t}(t_r-1)] = \delta(t_r-1) \tag{23-27}$$

that is, the effluent is an impulse that is delayed from the input impulse by $t_r = 1$ or $t = \bar{t}$.

Multistage CSTR This model has a particular importance because its RTD curve is bell-shaped like those of many experimental RTDs of packed beds and some empty tubes. The RTD is found by induction by solving the equations of one stage, two stages, and so on, with the result,

$$E(t_r) = \frac{C_n}{C^0} = \frac{n^n}{(n-1)!}\, t_r^{n-1} \exp(-nt_r) \tag{23-28}$$

Step response is found by integration, thus

$$F(t_r) = \int_0^{t_r} E(t_r)\, dt_r = 1 - \exp(-nt_r) \sum_{j=0}^{n-1} \frac{(nt_r)^j}{j!} \tag{23-29}$$

Plots of $E(t_r)$ and $f(t_r)$ for various values of n appear in Fig. 23-9. The bell shapes of $E(t_r)$ are more distinctive. The experimental curves of Figs. 23-10 and 23-11 clearly are of that family.

The peak of the E curve is reached at $t_r = (n-1)/n$ and has a magnitude

$$E(t_r)_{\max} = \frac{n(n-1)^{n-1}}{(n-1)!} \exp(1-n) \tag{23-30}$$

from which n can be found when $E(t_r)_{\max}$ has been measured.

Another significant characeristic of the E curve is the variance or the second moment which is

$$\sigma^2(t_r) = \int_0^{\infty} (t_r-1)^2 E(t_r)\, dt_r = \frac{1}{n} \tag{23-31}$$

The E equation can be rearranged into a linear form,

$$\ln[t_r E(t_r)] = \ln\left[\frac{n^n}{(n-1)!}\right] + n \ln[t_r \exp(-nt_r)] \tag{23-32}$$

With appropriate coordinates the slope of a loglog plot is n.

Combined Models, Transfer Functions The transfer function relation is

$$\overline{C}_{\text{output}} = (\text{Transfer function})\, \overline{C}_{\text{input}}$$
$$= G(s)\overline{C}_{\text{input}} \tag{23-33}$$

Some common transfer functions are

Element	*Transfer function, $G(s)$*
Ideal CSTR	$\dfrac{1}{(1+\bar{t}s)}$
PFR	$\exp(-\bar{t}s)$
n-stage CSTR (Erlang)	$\dfrac{1}{(1+\bar{t}s)^n}$
Erlang with time delay	$\dfrac{\exp(-\bar{t}_1 s)}{(1+\bar{t}_2 s)^n}$

The last item is of a PFR and an n-stage CSTR in series.

Although a transfer function relation may not be always invertible analytically, it has value in that the moments of the RTD may be derived from it, and it is thus able to represent an RTD curve. For instance, if G_0' and G_0'' are the limits of the first and second derivatives of the transfer function $G(s)$ as $s \Rightarrow 0$, the variance is

$$\sigma^2(t) = G_0'' - (G_0')^2$$

Characterization of RTD Curves An empirical RTD curve can be represented by equations of more than one algebraic form. The characteristic bell shape of many RTDs is evident in the real examples of Figs. 23-10 and 23-11. Such shapes invite comparison with some well-known statistical distributions and representation of the RTDs by their equations. Many of the standard statistical distributions are described by Hahn and Shapiro (*Statistical Models in Engineering*, Wiley, 1967) with their applicabilities. The most useful models in the present area are the gamma (or Erlang) and the Gaussian together with its Gram-Charlier extension. These distributions are representable by only a few parameters that define the asymmetry, the peak, and the shape in the vicinity of the peak. The moments—variance, skewness, and kurtosis—are such parameters.

Gamma or Erlang Distribution For nonintegral values, the factorial of the function $E(t_r)$ of Eq. (23-28) replaced as $(n-1)! = \Gamma(n)$. The result is called the gamma distribution,

$$E(t_r)_{\text{gamma}} = \frac{n^n}{\Gamma(n)}\, t_r^{n-1} \exp(-nt_r) \tag{23-34}$$

The value of n is the only parameter in this equation. Several procedures can be used to find its value when the RTD is known by experiment or calculation: from the variance, as in $n = 1/\sigma^2(t_r) = 1/\bar{t}^2\sigma^2(t)$, or from a suitable loglog plot or the peak of the curve as explained for the CSTR battery model. The Peclet number for dispersion is also related to n, and may be obtainable from correlations of operating variables.

Gaussian Distribution The best-known statistical distribution is the normal, or Gaussian, whose equation is

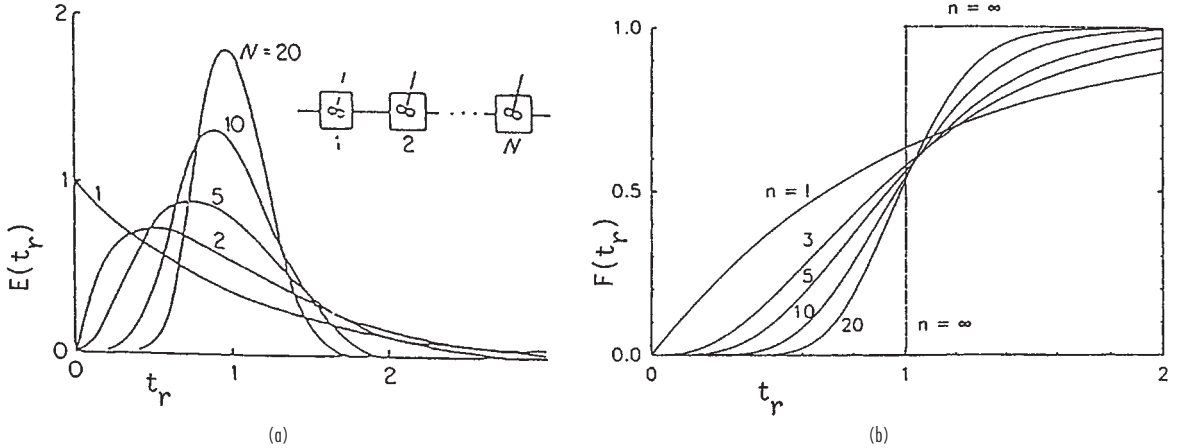


FIG. 23-9 Tracer responses to n-stage continuous stirred tank batteries; the Erlang model: (*a*) impulse inputs, (*b*) step input.

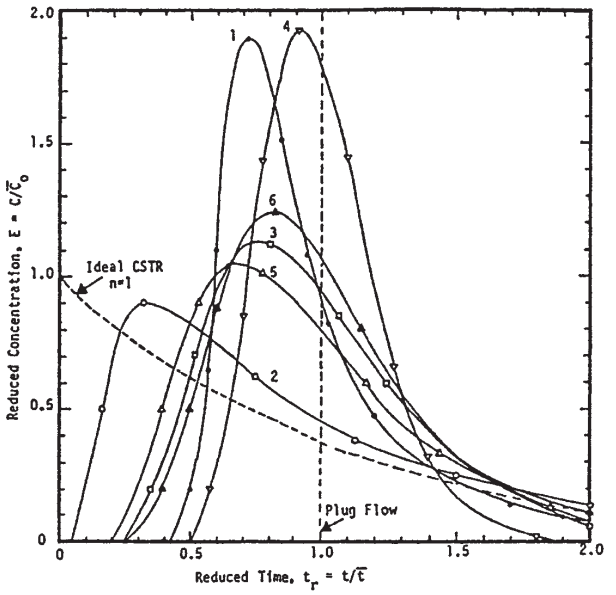


FIG. 23-10 Residence time distributions of pilot and commercial reactors. σ^2 = variance of the residence time distribution, n = number of stirred tanks with the same variance, Pe = Peclet number.

No.	Code	Process	σ^2	n	Pe
1	○	Aldolization of butyraldehyde	0.050	20.0	39.0
2	●	Olefin oxonation pilot plant	0.663	1.5	1.4
3	□	Hydrodesulfurization pilot plant	0.181	5.5	9.9
4	▽	Low-temp hydroisomerization pilot	0.046	21.6	42.2
5	△	Commercial hydrofiner	0.251	4.0	6.8
6	▲	Pilot plant hydrofiner	0.140	7.2	13.2

(*Walas,* Chemical Process Equipment, *Butterworths, 1990.*)

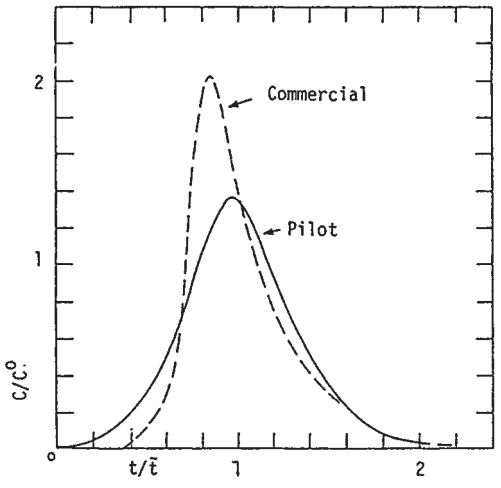


FIG. 23-11 Tracer tests on hydrodesulfurizers with 10-mm catalyst pellets. Commercial, 3 ft by 30 ft, $\bar{t}$ = 23 s, n = 12.9. Pilot, 4 in by 9 ft, $\bar{t}$ = 14 s, n = 9.3. To convert ft to m, multiply by 0.3048. (*Sherwood,* A Course in Process Design, *MIT Press, 1963.*)

$$C(t_r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(t_r-1)^2}{2\sigma^2}\right], \qquad -\infty \le t_r \le +\infty \tag{23-35}$$

Since only positive values of t_r are of concern in RTD work, this function is normalized by dividing by the integral from 0 to ∞ with the result

$$E(t_r)_{\text{gauss}} = f(\sigma) \exp\left[-\frac{(t_r-1)^2}{2\sigma^2}\right] \tag{23-36}$$

where

$$f(\sigma) = \frac{\sqrt{2/\pi\sigma^2}}{1 + \text{erf}\,(1/\sigma\sqrt{2})} \tag{23-37}$$

Gram-Charlier Series This is an infinite series whose coefficients involve the Gaussian distribution and its derivatives (Kendall, *Advanced Theory of Statistics,* vol. 1, Griffin, 1958). The derivatives, in turn, are expressed in terms of the moments. The series truncated at the coefficient involving the fourth moment is

$$E(t_r)_{\text{GC}} = E(t_r)_{\text{gauss}}\left[\frac{1 - m_3(3z - z^3)}{6} + \frac{(m_4 - 3)\,(z^4 - 6z^2 + 3)}{24}\right] \tag{23-38}$$

where $z = \dfrac{(t_r - 1)}{\sigma}$

$$m_3 = \left(\frac{\gamma}{\sigma}\right)^3 = \int_0^\infty \left(\frac{t_r - 1}{\sigma}\right)^3 E(t_r)\, dt_r$$

$$m_4 = \left(\frac{\delta}{\sigma}\right)^4 = \int_0^\infty \left(\frac{t_r - 1}{\sigma}\right)^4 E(t_r)\, dt_r$$

More terms of the series are usually not justifiable because the higher moments cannot be evaluated with sufficient accuracy from experimental data. A comparison of the fourth-order GC with other distributions is shown in Fig. 23-12, along with calculated segregated conversions of a first-order reaction. In this case, the GC is the best fit to the original. At large variances the finite value of the ordinate at $t_r = 0$ appears to be a fatal objection to both the Gaussian and GC distributions. On the whole, the gamma distribution is perhaps the best representation of experimental RTDs.

Empirical Equations Tabular (C,t) data are easier to use when put in the form of an algebraic equation. Then necessary integrals and derivatives can be formed most readily and accurately. The calculation of chemical conversions by such mechanisms as segregation, maximum mixedness, or dispersion also is easier with data in the form of equations.

Procedures for curve fitting by polynomials are widely available. Bell-shaped curves, however, are fitted better and with fewer constants by ratios of polynomials. For figuring chemical conversions, the

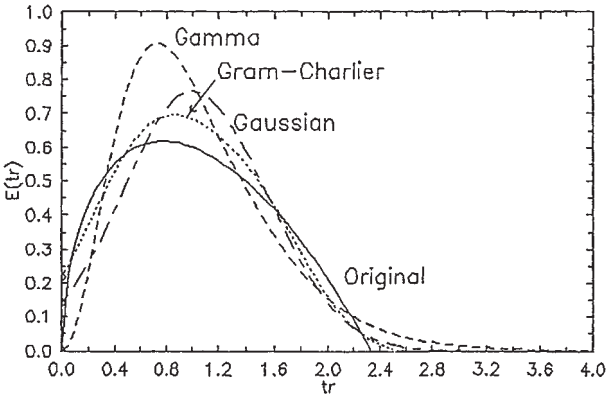


FIG. 23-12 Comparison of RTD models, all with the same variance and skewness. Values of C/C_0 of segregated conversion of a first-order reaction with $k\bar{t}$ = 3: original, 0.1408; gamma, 0.1158; Gauss, 0.1148; GC, 0.1418.

curve fit need not be accurate at small values of $E(t)$, since those regions do not affect the overall conversion significantly.

CHEMICAL CONVERSION

A distinction is to be drawn between situations in which (1) the flow pattern is known in detail, and (2) only the residence time distribution is known or can be calculated from tracer response data. Different networks of reactor elements can have similar RTDs, but fixing the network also fixes the RTD. Accordingly, reaction conversions in a known network will be unique for any form of rate equation, whereas conversions figured when only the RTD is known proceed uniquely only for linear kinetics, although they can be bracketed in the general case.

When the flow pattern is known, conversion in a known network and flow pattern is evaluated from appropriate material and energy balances. For first-order irreversible isothermal reactions, the conversion equation can be obtained from the transfer function by replacing s with the specific rate k. Thus, if $G(s) = \bar{C}/\bar{C}_0 = 1/(1 + \bar{t}s)$, then $C/C_0 = 1/(1 + k\bar{t})$. Complete knowledge of a network enables incorporation of energy balances into the solution, whereas the RTD approach cannot do that.

Segregated Flow In segregated flow the molecules travel as distinct groups, in which all molecules that enter the vessel together leave together. The groups are small enough so that the RTD of the whole system is represented by a smooth curve. For reaction orders above one, with a given RTD, the conversion is a maximum in segregated flow and a minimum under *maximum mixedness* conditions. This point is discussed in detail later.

Each group of molecules reacts independently of any other group, that is, as a batch reactor. Batch conversion equations for power law rate equations are:

$$\left(\frac{C}{C_0}\right)_{\text{batch}} = \exp(-kt) = \exp(-k\bar{t}t_r), \qquad \text{first order} \tag{23-39}$$

$$\left[\frac{1}{1 + (q-1)kC^{q-1}\bar{t}t_r}\right]^{1/(q-1)}, \qquad \text{order } q \tag{23-40}$$

For other rate equations a numerical solution may be needed.

The mean conversion of all the groups is the sum of the products of the individual conversions and their volume fractions of the total flow. Since the groups are small, the sum is replaced by the integal. Thus,

$$\left(\frac{C}{C_0}\right)_{\text{segregated}} = \int_0^\infty \left(\frac{C}{C_0}\right)_{\text{batch}} E(t)\,dt \tag{23-41}$$

$$= \int_0^\infty \left(\frac{C}{C_0}\right)_{\text{batch}} E(t_r)\,dt_r \tag{23-42}$$

Conversion in segregated flow is less than in plug flow and somewhat greater than in a CSTR battery with the same variance of the RTD.

When a conversion and an RTD are known, the specific rate can be found by trial: Values of k are estimated until one is found that makes the segregated integral equal to the known value. Moreover, if a series of conversions are known at several residence times, the order of the reaction can be found by trying different orders and noting which give a constant series of specific rates. A catch here, however, is that the RTD depends on the hydrodynamics of the process and may change with the residence time.

Maximum Mixedness The flow pattern for maximum mixedness is compared with segregated flow in Fig. 23-13. Segregated flow is in a vessel with multiple side *outlets* that result in a particular RTD. Maximum mixedness occurs in a plug flow vessel with multiple side *inlets* whose flow pattern is given by the same RTD. The main flow in the vessel is plug flow, but at each inlet the incoming material is completely mixed across the cross section with the axial flow. This means that each portion of fresh material is mixed with all the material that has the same life expectation, regardless of the actual residence time in the vessel up to the time of mixing. The life expectation under plug flow conditions is measured by the distance remaining to be traveled before leaving the vessel.

In contrast to segregated flow, in which the mixing occurs only after each sidestream leaves the vessel, under maximum mixedness mixing of all molecules having a certain period remaining in the vessel (the life expectation) occurs at the time of introduction of fresh material. These two mixing extremes—as late as possible and as soon as possible, both consistent with the same RTD—correspond to performance extremes of the vessel as a chemical reactor.

The differential equation of maximum mixedness was obtained by Zwietering (*Chem. Eng. Sci.*, **11,** 1 [1959]). It is:

$$\frac{dC}{dt} = R_c - \frac{E(t)}{1 - F(t)}(C_0 - C) \tag{23-43}$$

where R_c is the chemical rate equation; for an order q, $R_c = kC^q$. In the normalized units $f = C/C_0$ and $t_r = t/\bar{t}$,

$$\frac{df}{dt_r} = k\bar{t}C_0^{q-1}f^q - \frac{E(t_r)}{1 - F(t_r)}(1 - f) \tag{23-44}$$

The boundary condition is

$$\frac{df}{dt_r} = 0 \qquad \text{for} \qquad t_r \Rightarrow \infty \tag{23-45}$$

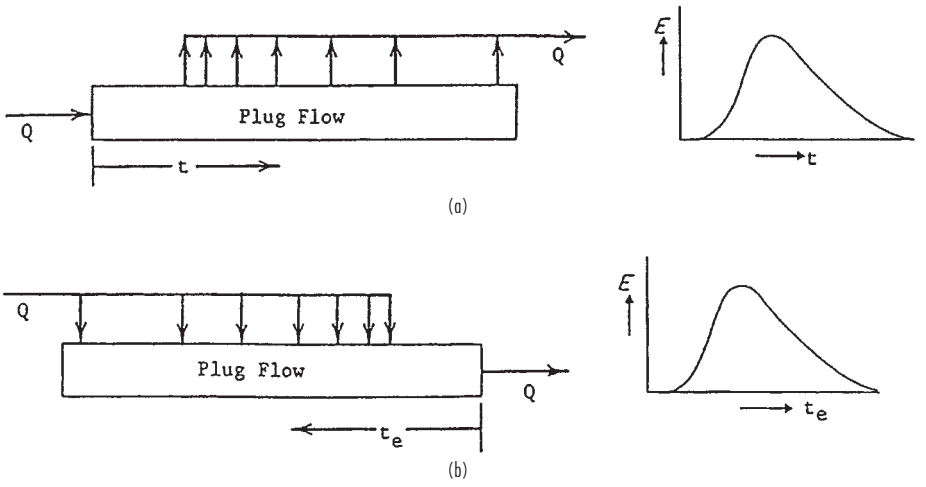


FIG. 23-13 The two limiting flow patterns with the same RTD. (*a*) Segregated flow, in which all molecules of any exit stream have the same residence time. (*b*) Maximum mixed flow, in which all molecules of an external stream with a certain life expectation are mixed with all molecules of the internal stream that have the same life expectation.

which makes

$$k\bar{t}C_0^{q-1}f_\infty^q - \frac{E(\infty)}{1-F(\infty)}(1-f_\infty) = 0 \qquad (23\text{-}46)$$

The conversion achieved in the vessel is obtained by the solution of the differential equation at the exit of the vessel where the life expectation is $t = 0$. The starting point for the integration is (f_∞, t_∞). When integrating numerically, however, the RTD becomes essentially 0 by the time t_r becomes 3 or 4, and the value of the integral beyond that point becomes nil. Accordingly, the integration interval is from $(f_\infty, t_r \le 3 \text{ or } 4)$ to $(f_{\text{effluent}}, t_r = 0)$. f_∞ is found from Eq. (23-46).

Numerical solutions of the maximum mixedness and segregated flow equations for the Erlang model have been obtained by Novosad and Thyn (*Coll. Czech. Chem. Comm.*, **31,** 3,710–3,720 [1966]). A few comparisons are made in Fig. 23-14. In some ranges of the parameters n or R_c the differences in conversion or reactor sizes for the same conversions are substantial. On the basis of only an RTD for the flow pattern, perhaps only an average of the two calculated extreme performances is justifiable.

Experimental confirmations of these mixing mechanisms are scarce. One study was with a 50-gal stirred tank reactor (Worrell and Eagleton, *Can. J. Chem. Eng.*, 254–258 [Dec. 1964]). They found seg-

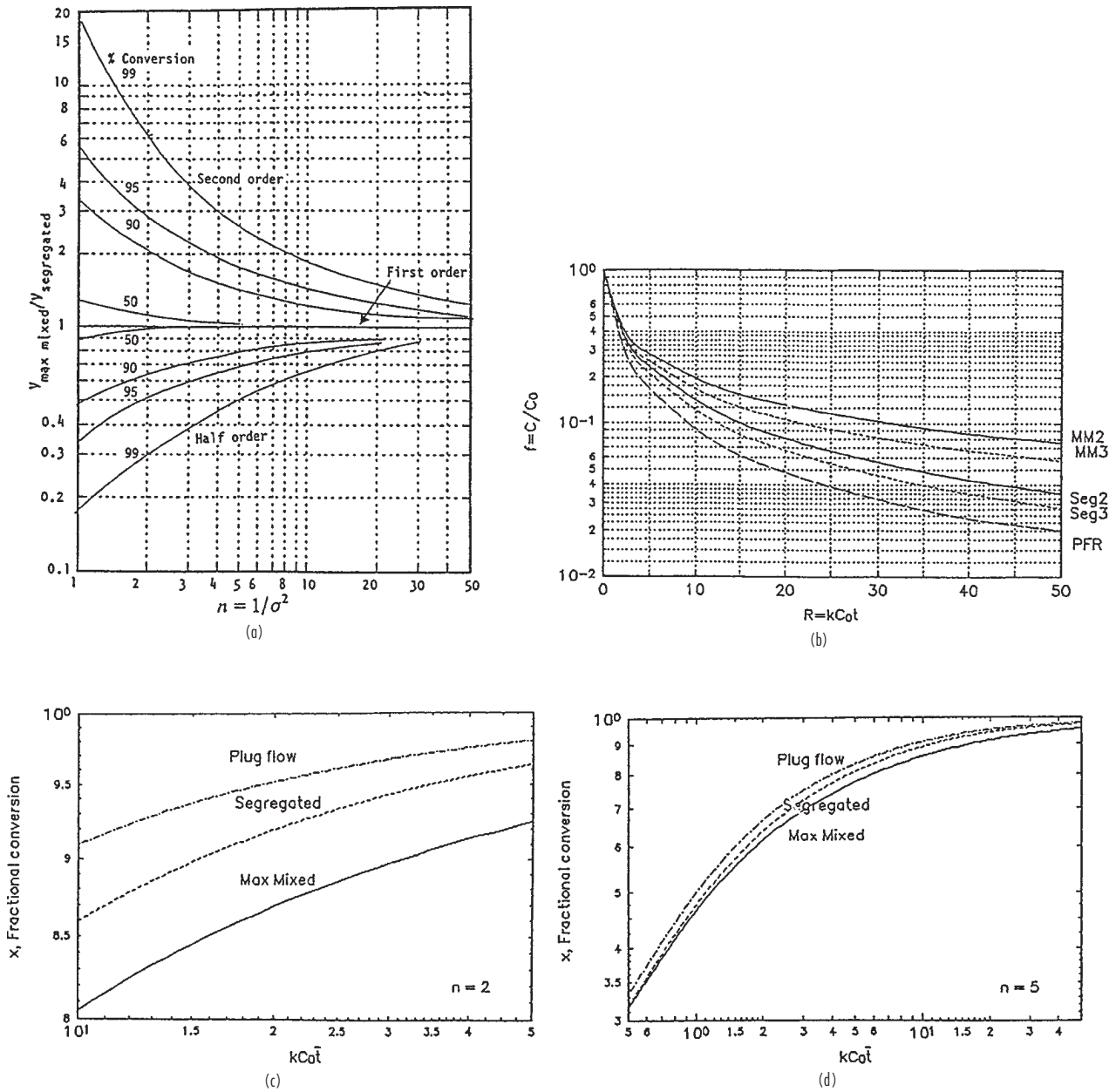


FIG. 23-14 Comparison of maximum mixed, segregated, and plug flows. (*a*) Relative volumes as functions of variance or n, for several reaction orders. (*b*) Second-order reaction with $n = 2$ or 3. (*c*) Second-order, $n = 2$. (*d*) Second-order, $n = 5$.

regation at low agitation, and were able to correlate complete mixing and maximum mixedness in terms of the power input and recirculation within the vessel.

Dispersion Model An impulse input to a stream flowing through a vessel may spread axially because of a combination of molecular diffusion and eddy currents that together are called *dispersion.* Mathematically, the process can be represented by Fick's equation with a dispersion coefficient replacing the diffusion coefficient. The dispersion coefficient D_e is associated with a linear dimension L and a linear velocity in the Peclet number, $\text{Pe} = uL/D_e$. In plug flow, $D_e = 0$ and $\text{Pe} \Rightarrow \infty$; and in a CSTR, $D_e \Rightarrow \infty$ and $\text{Pe} = 0$.

The dispersion coefficient is orders of magnitude larger than the molecular diffusion coefficient. Some rough correlations of the Peclet number are proposed by Wen (in Petho and Noble, eds., *Residence Time Distribution Theory in Chemical Engineering,* Verlag Chemie, 1982), including some for fluidized beds. Those for axial dispersion are:

1. Axial dispersion in empty tubes,

$$\frac{1}{\text{Pe}} = \frac{1}{(\text{Re})(\text{Sc})} + \frac{(\text{Re})(\text{Sc})}{192}, \qquad 1 \le \text{Re} \le 2000, \quad 0.2 \le \text{Sc} \le 1000 \tag{23-47}$$

$$\frac{1}{\text{Pe}} = \frac{3(10^7)}{(\text{Re})^{2.1}} + \frac{1.35}{(\text{Re})^{0.125}}, \qquad \text{Re} \ge 2000 \tag{23-48}$$

2. Axial dispersion of gases in packed tubes,

$$\frac{1}{\text{Pe}} = \frac{0.3}{(\text{Re})(\text{Sc})} + \frac{0.5}{1 + \dfrac{3.8}{(\text{Re})(\text{Sc})}}, \qquad 0.008 \le \text{Re} \le 400, \quad 0.28 \le \text{Sc} \le 2.2 \tag{23-49}$$

where Pe = Peclet number, $d_p u_0/\varepsilon D$
Re = Reynolds number, $d_p s_p u_0/\nu$
Sc = Schmidt number, ν/D
D = axial dispersion coefficient
d_p = Diameter of particle or empty tube
ε = Fraction voids in packed bed
u_0 = Superficial velocity in the vessel.

In a vessel with axial dispersion, the steady-state equation for a reaction of order q is

$$\frac{d^2f}{dz^2} = \text{Pe}\left(\frac{df}{dz} - R_c\right) = \text{Pe}\left(\frac{df}{dz} - k\bar{t}C_0^{q-1}f^q\right) \tag{23-50}$$

where the normalized variables are $f = C/C_0$ and $z = x/L$. For tracer flow, $R_c = 0$ and the time derivative appears,

$$\frac{\partial f}{\partial t_r} = \frac{1}{\text{Pe}}\frac{\partial^2 f}{\partial z^2} - \frac{\partial f}{\partial z} \tag{23-51}$$

The solution of this partial differential equation is recorded in the literature (Otake and Kunigata, *Kagaku Kogaku,* **22,** 144 [1958]). The plots of $E(t_r)$ against t_r are bell-shaped, resembling the corresponding Erlang plots. A relation is cited later between the Peclet number, n_{erlang}, and $\sigma^2(t_r)$.

Boundary Conditions In normal operation with "closed ends," reactant is brought in by bulk flow and carried away by both bulk and dispersion flow. At the inlet where $L = 0$ or $z = 0$,

$$uC_0 = \left(uC - D\frac{\partial C}{\partial L}\right)_{L=0} \tag{23-52}$$

or

$$f_0 = \left(f - \frac{1}{\text{Pe}}\frac{\partial f}{\partial z}\right)_{z=0} \tag{23-53}$$

At the exit where $z = 1$,

$$\left(\frac{\partial f}{\partial z}\right)_{z=1} = 0 \tag{23-54}$$

With these two-point boundary conditions the dispersion equation, Eq. (23-50), may be integrated by the *shooting method.* Numerical solutions for first- and second-order reactions are plotted in Fig. 23-15.

The discontinuity of concentration at the inlet is commonly observed with CSTR operations, where Pe = 0. At other values of Pe, the effects are shown in Fig. 23-16.

Comparison of Models Only scattered and inconclusive results have been obtained by calculation of the relative performances of the different models as converters. Both the RTD and the dispersion coefficient require tracer tests for their accurate determination, so neither method can be said to be easier to apply. The exception is when one of the cited correlations of Peclet numbers in terms of other groups can be used, although they are rough. The tanks-in-series model, however, provides a mechanism that is readily visualized and is therefore popular.

The Erlang (or gamma) and dispersion models can be related by equating the variances of their respective $E(t_r)$ functions. The result for the "closed-ends" condition is

$$\sigma^2(t_r) = \frac{2[\text{Pe} - 1 + \exp(-\text{Pe})]}{\text{Pe}^2} \tag{23-55}$$

$$= \frac{1}{n_{\text{erlang}}} \tag{23-56}$$

For both large and small values of Pe,

$$n_{\text{erlang}} \Rightarrow \frac{\text{Pe}}{2} \tag{23-57}$$

MULTIPLICITY AND STABILITY

Normally, when a small change is made in the condition of a reactor, only a comparatively small change in the response occurs. Such a system is uniquely stable. In some cases, a small positive perturbation can result in an abrupt change to one steady state, and a small negative perturbation to a different steady condition. Such multiplicities occur most commonly in variable temperature CSTRs. Also, there are cases where a process occurring in a porous catalyst may have more than one effectiveness at the same Thiele number and thermal balance. Some isothermal systems likewise can have multiplicities, for instance, CSTRs with rate equations that have a maximum, as in Example (*d*) following.

Conditions at steady state are determined by heat and material balances. Such balances for a CSTR can be put in the form,

Heat generated by reaction = Sensible heat pickup

or

$$-\Delta H_r V_r r_c = V'\rho C_p(T - T_f) \tag{23-58}$$

Four examples of multiplicity and stability follow.

Example (a) For a first-order reaction in a CSTR, the rate of reaction is:

$$r_c = kC = \frac{kC_f}{1 + k\bar{t}} = \frac{C_f \exp(a + b/T)}{1 + \bar{t}\exp(a + b/T)}$$

When this is substituted into the previous equation, both sides become functions of T and may be plotted against each other. As Fig. 23-17 of a typical case shows, as many as three steady states are possible. When generation is greater than removal (as at points A– and B+), the temperature will rise to the next higher steady state; when generation is less than removal (as at points A+ and B–), it will fall to the next steady state. Point B is an unsteady state, while A and C are steady.

Example (b) In terms of fractional conversion, $f = 1 - C/C_f$, the material and energy balances for a first-order CSTR are:

$$f = \frac{k\bar{t}}{1 + k\bar{t}} = \frac{50k}{1 + 50k} = \frac{\rho C_p(T - T_f)}{-\Delta H_r C_f} = \frac{1.2(0.9)(T - T_f)}{46{,}000C_f}$$

The two equations are plotted for several combinations of C_f and T_f. The number of steady states can be one, two, or three if zero or complete conversion are considered possibilities.

Example (c) For the reactions $A \overset{1}{\Rightarrow} B \overset{2}{\Rightarrow} C$ the concentrations are:

$$A = \frac{A_f}{1 + k_1\bar{t}}, \qquad B = \frac{k_1\bar{t}A_f}{(1 + k_1\bar{t}(1 + k_2\bar{t})}$$

The heat balance is:

$$-\Delta H_a(A_f - A) - \Delta H_b(B - B_f) = \rho C_p(T - T_f)$$

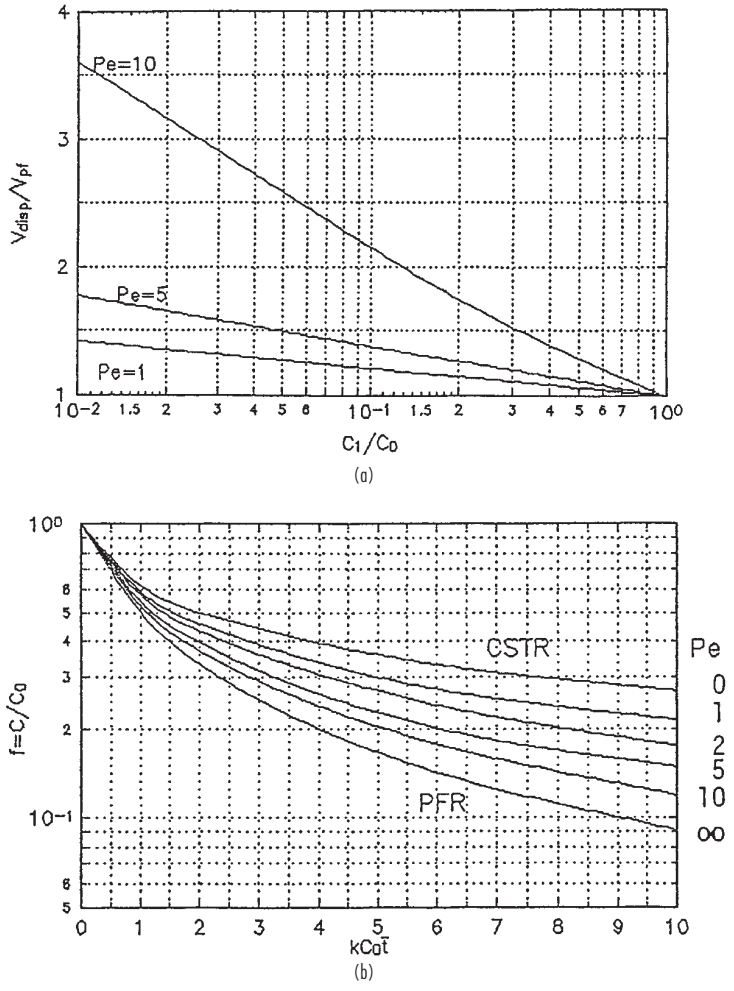


FIG. 23-15 Chemical conversion by the dispersion model. (*a*) First-order reaction, volume relative to plug flow against residual concentration ratio. (*b*) Second-order reaction, residual concentration ratio against $kC_0\bar{t}$.

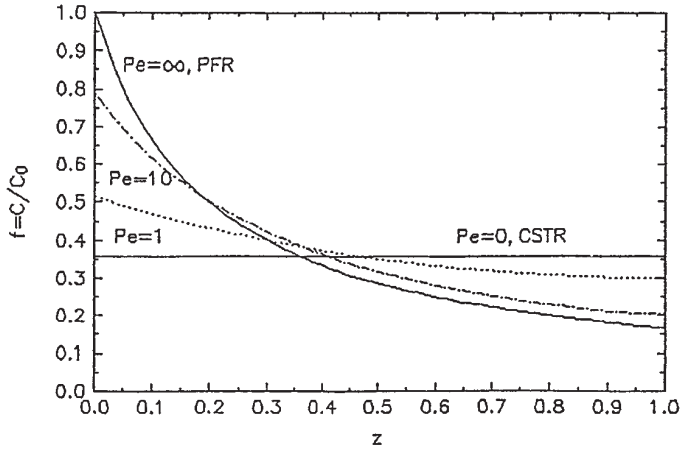


FIG. 23-16 Concentration jump at the inlet of a "closed ends" vessel with dispersion. Second-order reaction with $kC_0\bar{t} = 5$.

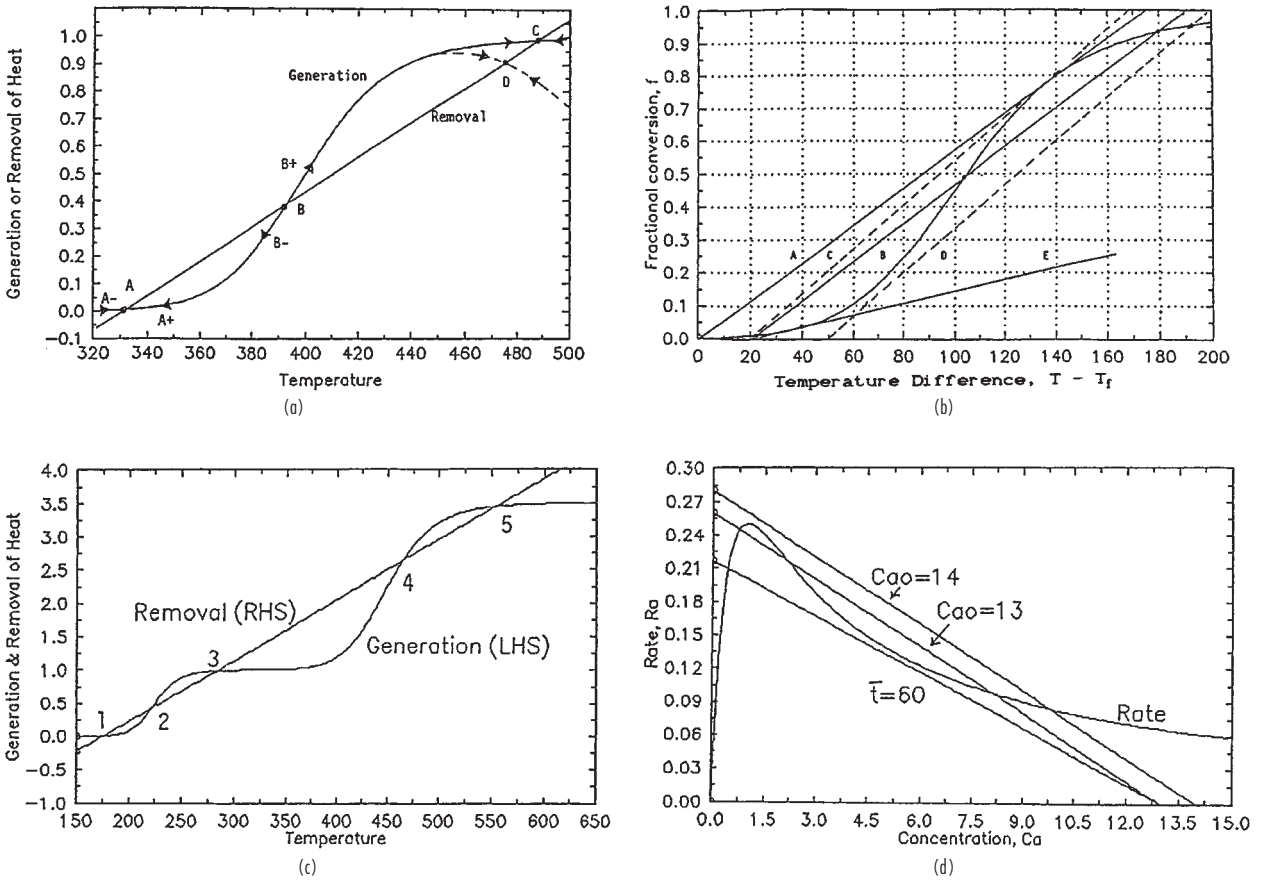


FIG. 23-17 Multiple steady states of CSTRs, stable and unstable, adiabatic except the last item. (*a*) First-order reaction, A and C stable, B unstable, A is no good for a reactor, the dashed line is of a reversible reaction. (*b*) One, two, or three steady states depending on the combination (C_f, T_f). (*c*) The reactions A ⇒ B ⇒ C, with five steady states, points 1, 3, and 5 stable. (*d*) Isothermal operation with the rate equation $r_a = C_a/(1 + C_a)^2 = (C_{a0} - C_a)/\bar{t}$.

In a specific case this becomes

$$110\left(\frac{k_1\bar{t}}{1+k_1\bar{t}}\right)\left(\frac{1+2.5k_2\bar{t}}{1+k_2\bar{t}}\right) = T - 175$$

with $k_1\bar{t} = \exp(20 - 4{,}500/T)$ and $k_2\bar{t} = \exp(20 - 9{,}000/T)$. The plot shows 5 steady states, of which 1, 3, and 5 are stable. T is in K.

Example (d) The rate equation and the CSTR material balance of this process are:

$$r_a = \frac{C_a}{(1+C_a)^2} = \frac{C_{a0} - C_a}{\bar{t}}$$

The plots of these equations with $C_{a0} = 13$ and $\bar{t} = 50$ show three intersections, and only one with $C_{a0} = 14$, but the conversion is poor. Keeping $C_{a0} = 13$ but making $\bar{t} = 60$ changes the stable operation to $C_a = 0.6$, or 95 percent conversion.

Instances of multiplicities in CSTR batteries and in PFRs also can be developed.

Only a very few experimental studies have been made for detection of multiplicities of steady states to check on theoretical predictions. The studies of multiplicities and of oscillations of concentrations have similar mathematical bases. Comprehensive reviews of these topics are by Schmitz (*Adv. Chem. Ser.*, **148,** 156, ACS [1975]), Razon and Schmitz (*Chem. Eng. Sci.*, **42,** 1,005–1,047 [1987]), Morbidelli, Varma, and Aris (in Carberry and Varma, eds., *Chemical Reaction and Reactor Engineering,* Dekker, 1987, pp. 975–1,054).

CATALYSIS

A catalyst is a substance that increases the rate of a reaction by participating chemically in intermediate stages of reaction and is ultimately liberated in a chemically unchanged form. Over a period of time, however, permanent changes in the catalyst—deactivation—may occur. *Inhibitors* are substances that slow down rates of reaction. The turnover ratio, the number of molecules converted per molecule of catalyst, can be in the millions. Many catalysts have specific actions in that they influence only one reaction or group of definite reactions. The outstanding example is the living cell in which there are several hundred catalysts, called *enzymes,* each one favoring a specific chemical process. When a reaction can proceed by more than one path, a particular catalyst may favor one path over another and thus lead to a product distribution different from an uncatalyzed reaction. A catalytic reaction requires a lower energy of activation, thus permitting a reduction of temperature at which the reaction can proceed favorably. The equilibrium condition is not changed since both forward and reverse rates are accelerated equally. For example, a good hydrogenation catalyst also is a suitable dehydrogenation accelerator but possibly with a different most-favorable temperature.

Catalytic processes may be homogeneous in the liquid or gas phase (for instance, nitrogen oxides in the Chamber process for sulfuric acid), but industrial examples are most often heterogeneous with a

solid catalyst and fluid reactants. Some large industrial reactors of this type are illustrated in Fig. 23-18.

HOMOGENEOUS CATALYSIS

The most numerous cases of homogeneous catalysis are by certain ions or metal coordination compounds in aqueous solution and in biochemistry, where enzymes function catalytically. Many ionic effects are known. The hydronium ion H_3O^+ and the hydroxyl ion OH^- catalyze hydrolyses such as those of esters; ferrous ion catalyzes the decomposition of hydrogen peroxide; decomposition of nitramide is catalyzed by acetate ion. Other instances are inversion of sucrose by HCl, halogenation of acetone by H^+ and OH^-, hydration of isobutene by acids, hydrolysis of esters by acids, and others.

The specific action of a particular metal complex can be altered by varying the ligands or coordination number of the complex or the oxidation state of the central metal atom.

Probable mechanisms often have been deduced: The reactant forms a short-lived intermediate with the catalyst that subsequently decomposes into the product and regenerated catalyst. In fluid phases such intermediates can be detected spectroscopically. This is in contrast to solid catalysis, where the detection of intermediates is much more difficult and is not often accomplished.

Significant characteristics of homogeneous catalysis are that they are highly specific and proceed under relatively mild conditions—again in contrast to solid catalysis, which is less discriminating as to reaction and may require extremes of temperature and pressure. A problem with homogeneous operation is the difficulty of separating product and catalyst.

A review of industrial processes that employ homogeneous catalysts is by Jennings, ed. (*Selected Developments in Catalysis,* Blackwell Scientific, 1985). Some of those processes are:

- Alkylation of isobutane with C_3-C_4 olefins in the presence of HF at 25 to 35°C or 90 to 98% sulfuric acid at 10°C (50°F).
- Alkylation of isobutane and ethylene with a complex of liquid hydrocarbon + $AlCl_3$ + HCl.
- The Wacker process for the oxidation of ethylene to acetaldehyde with $PdCl_2/CuCl_2$ at 100°C (212°F) with 95 percent yield and 95 to 99 percent conversion per pass.
- The OXO process for higher alcohols: CO + H_2 + C_3H_6 ⇒ *n*-butanal ⇒ further processing. Catalyst is rhodium triphenylphosphine coordination compound, 100°C (212°F), 30 atm (441 psi).
- Acetic acid from methanol by the Monsanto process, CH_3OH + CO ⇒ CH_3COOH, rhodium iodide catalyst, 3 atm (44 psi), 150°C (302°F), 99 percent selectivity of methanol.
- Ammonia is a cyclic reagent that is recovered by the end of the Solvay process for sodium carbonate from lime and salt. Although there is nothing obscure about the intermediate reactions, ammonia definitely participates in a catalytic sequence.

Immobilized or Polymer Bound, or Heterogenized Catalysts The specificity of homogeneous and separability of solid catalysts are realized by attaching the catalyst to a solid support. This is commonly done for enzymes. In use as carriers are organic polymers such as polystyrene and inorganic polymers such as zeolites, silica, or alumina. A catalyst metal atom, for instance, is anchored to the polymer through a group that is chemically bound to the polymer with a coordinating site such as $-P(C_6H_5)_2$ or $-C_5H_4$ (cyclopentadienyl). Immobilized catalysts have applications in hydrogenation, hydroformylation, and polymerization reactions (Lieto and Gates, *CHEMTECH,* 46–53 [Jan. 1983]).

Phase-Transfer Catalysis In phase-transfer catalysis (PTC), reactions between reactants located in different phases (typically organic and aqueous liquids) are brought about or accelerated by a catalyst that migrates between the phases. Ultimately, the reaction takes place in the organic phase. Although no one mechanism explains everything, the catalyst may combine with a reactant in one phase, migrate to the other phase in which it is also miscible, and react there. Ultimately, the reaction is homogeneous. The catalysts used most extensively are quaternary ammonium or phosphonium salts and crown ethers and cryptates, for instance benzyltriethylammonium chloride and the cheaper methyltrioctylammonium chloride. Reactions helped by PTC include making higher esters, ethers, and alkylates, polymerization of butyl acrylate, and oxidation of olefins with $KMnO_4$. In most of these instances the reaction rate is nil without the catalyst (Dehmlow, *Phase Transfer Catalysis,* Verlag Chemie, 1992).

Effect of Concentration All catalytic reactions appear to involve the formation of intermediate compounds with the catalyst. For a reactant A, product B, and catalyst the corresponding equation is

$$A + C \Rightarrow AC \Rightarrow B + C$$

When the first step is rate controling,

$$r_a = k[A][C]^\alpha$$

In some cases, the exponent is unity. In other cases, the simple power law is only an approximation for an actual sequence of reactions. For instance, the chlorination of toluene catalyzed by acids was found to have $\alpha = 1.15$ at 6°C (43°F) and 1.57 at 32°C (90°F), indicating some complex mechanism sensitive to temperature. A particular reaction may proceed in the absence of catalyst but at a reduced rate. Then the rate equation may be

$$r_a = (k_1 + k_2[C]^\alpha)[A]$$

An instance of *autocatalysis* is the hydrolysis of methyl acetate, which is catalyzed by product acetic acid, A ⇒ C. The rate equation may be

$$r_a = k[A][C] = k[A][A_0 - A]$$

which will have a maximum value that is characteristic of autocatalytic reactions in general.

CATALYSIS BY SOLIDS

Solid catalysts are widely employed because they are usually cheap, are easily separated from the reaction medium, and are adaptable to either flow or nonflow reactors. Their drawbacks are lack of specificity and possibly high temperatures and pressures.

Usually they are employed as porous pellets in a packed bed. Some exceptions are platinum for the oxidation of ammonia, which is in the form of several layers of fine-mesh wire gauze, and catalysts deposited on membranes. Pore surfaces can be several hundred m^2/g and pore diameters of the order of 100 Å. The entire structure may be of catalytic material (silica or alumina, for instance, sometimes exert catalytic properties) or an active ingredient may be deposited on a porous refractory carrier as a thin film. In such cases the mass of expensive catalytic material, such as Pt or Pd, may be only a fraction of 1 percent.

The principal components of most solid catalysts are three in number:

1. A catalytically active substance or mixture.
2. A carrier of more or less large specific surface, often refractory to withstand high temperatures. A carrier may have some promotion action; for example, silica carrier helps chromia catalyst.
3. Promoters, usually present in small amount, which enhance activity or retard degradation; for instance, rhenium slows coking of platinum reforming, and KCl retards vaporization of $CuCl_2$ in oxychlorination for vinyl chloride.

Selection of Catalysts A basic catalyst often can be selected by using general principles, but the subsequent fine tuning of a commercially attractive recipe must be done experimentally. A start for catalyst design usually is by analogy to what is known to be effective in chemically similar problems, although a scientific basis is being developed. This involves a study in detail of the main possible intermediate reactions that could occur and of the proton and electron receptivity of the catalyst and possible promoters, as well as reactant bond lengths and crystal lattice dimensions. Several designs are made from this point of view by Trimm (*Design of Industrial Catalysts,* Elsevier, 1980). Some of this scientific basis is treated by Hegedus et al. (*Catalyst Design Progress and Perspectives,* Wiley, 1987). Preparation of specific catalysts is described by Stiles (*Catalyst Manufacture,* Dekker, 1983). A thorough coverage of catalytic reactions and catalysts arranged according to the periodic table is in a series by Roiter ed. (*Handbook of Catalytic Properties of Substances,* in Russian, 1968). Industrial catalyst practice is summarized by Thomas (*Cat-*

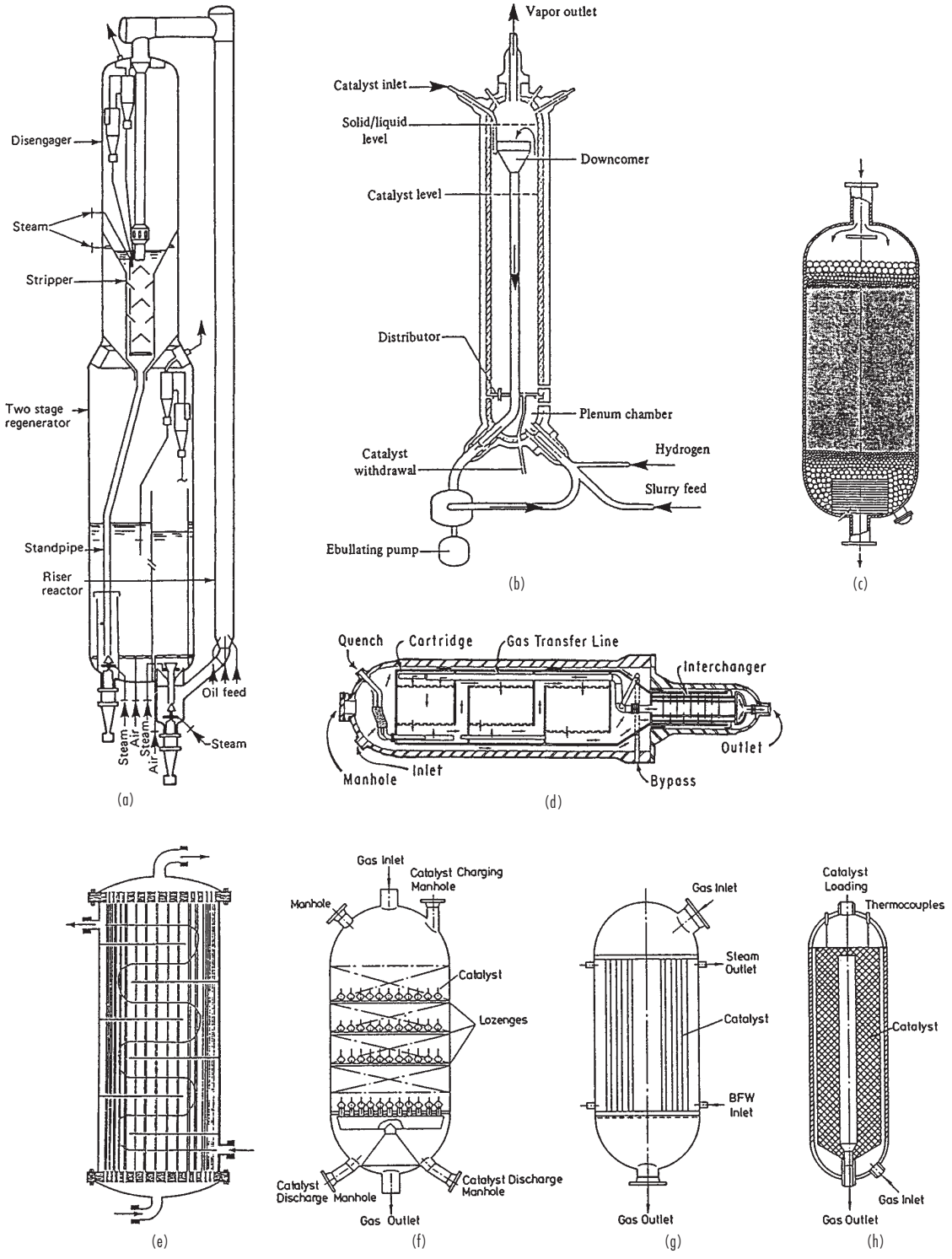


FIG. 23-18 Reactors with solid catalysts. (*a*) Riser cracker with fluidized zeolite catalyst, 540°C; circulation by density difference, 34 to 84 kg/m^3 in riser, 420 to 560 kg/m^2 in regenerator. (*b*) Ebullating fluidized bed for conversion of heavy stocks to gas and light oils. (*c*) Fixed bed unit with support and hold-down zones of larger spheres. (*d*) Horizontal ammonia synthesizer, 26 m long without the exchanger, 2,000 ton/d (*M W Kellogg Co.*). (*e*) Shell-and-tube vessel for hydrogenation of crotonaldehyde has 4,000 packed tubes, 30 mm ID, 10.7 m long, aldehyde feed 209 kg mol/h, hydrogen feed 2,090 kg mol/h. (*After Berty, in Leach,* ed., Applied Industrial Catalysis, *vol. 1, Academic Press, 1983, p. 51*). (*f*), (*g*), (*h*) Methanol synthesizers, 50 to 100 atm, 230 to 300°C, Cu catalyst; ICI quench type, Lurgi tubular, Haldor Topsoe radial flow (*Marschner and Moeller, in Leach, loc. cit.*). To convert ton/d to kg/h, multiply by 907; atm to kPa, multipy by 101.3.

alytic Processes and Proven Catalysts, Academic Press, 1970) who names manufacturers of catalysts for specific processes. Specific processes and general aspects of catalysts are covered by Leach, ed. (*Applied Industrial Catalysis,* 3 vols., Academic Press, 1983–1984). Many industrial processes are described by Gates et al. (*Chemistry of Catalytic Processes,* McGraw-Hill, 1979), Matar et al. (*Catalysis in Petrochemical Processes,* Kluwer Academic Publishers, 1989), Pines (*Chemistry of Catalytic Conversions of Hydrocarbons,* Academic Press, 1981) and Satterfield (*Heterogeneous Catalysis in Industrial Practice,* McGraw-Hill, 1991). Books and encyclopedia articles on particular chemicals and processes may be consulted for catalytic data. There are also eight journals devoted largely to catalytic kinetics.

Kinds of Catalysts To a certain extent it is known what kinds of reactions are speeded up by certain classes of catalysts, but individual members of the same class may differ greatly in activity, selectivity, resistance to deactivation, and cost. Since solid catalysts are not particularly selective, there is considerable crossing of lines in the classification of catalysts and the kinds of reactions they favor. Although some trade secrets are undoubtedly employed to obtain marginal improvements, the principal catalytic effects are known in many cases.

Strong acids are able to donate protons to a reactant and to take them back. Into this class fall the common acids, aluminum halides, and boron trifluoride. Also acid in nature are silica, alumina, aluminosilicates, metal sulfates and phosphates, and sulfonated ion exchange resins. They can transfer protons to hydrocarbons acting as weak bases. Zeolites are dehydrated aluminosilicates with small pores of narrow size distribution, to which is due their highly selective action since only molecules small enough to enter the pores can react.

Base catalysis is most effective with alkali metals dispersed on solid supports or, in the homogeneous form, as aldoxides, amides, and so on. Small amounts of promoters form organoalkali comnpounds that really contribute the catalytic power. Basic ion exchange resins also are useful. Base-catalyzed processes include isomerization and oligomerization of olefins, reactions of olefins with aromatics, and hydrogenation of polynuclear aromatics.

Metal oxides, sulfides, and hydrides form a transition between acid/base and metal catalysts. They catalyze hydrogenation/dehydrogenation as well as many of the reactions catalyzed by acids, such as cracking and isomerization. Their oxidation activity is related to the possibility of two valence states which allow oxygen to be released and reabsorbed alternately. Common examples are oxides of cobalt, iron, zinc, and chromium and hydrides of precious metals that can release hydrogen readily. Sulfide catalysts are more resistant than metals to the formation of coke deposits and to poisoning by sulfur compounds; their main application is in hydrodesulfurization.

Metals and alloys, the principal industrial metallic catalysts, are found in periodic group VIII, which are transition elements with almost-completed 3*d,* 4*d,* and 5*d* electronic orbits. According to theory, electrons from adsorbed molecules can fill the vacancies in the incomplete shells and thus make a chemical bond. What happens subsequently depends on the operating conditions. Platinum, palladium, and nickel form both hydrides and oxides; they are effective in hydrogenation (vegetable oils) and oxidation (ammonia or sulfur dioxide). Alloys do not always have catalytic properties intermediate between those of the component metals, since the surface condition may be different from the bulk and catalysis is a function of the surface condition. Addition of some rhenium to Pt/Al_2O_3 permits the use of lower temperatures and slows the deactivation rate. The mechanism of catalysis by alloys is still controversial in many instances.

Transition-metal organometallic catalysts in solution are more effective for hydrogenation than are metals such as platinum. They are used for reactions of carbon monoxide with olefins (hydroformylation) and for some oligomerizations. They are sometimes immobilized on polymer supports with phosphine groups.

Kinds of Catalyzed Organic Reactions A fundamental classification of organic reactions is possible on the basis of the kinds of bonds that are formed or destroyed and the natures of eliminations, substitutions, and additions of groups. Here a more pragmatic list of 20 commercially important kinds or classes of reactions will be discussed. In all instances of solid-catalyzed reactions, chemisorption is a primary step. Often molecules are dissociated on chemisorption into the more active atomic forms, for instance, of CO, H_2, N_2, and O_2 on platinum.

1. Alkylations—for example, of olefins with aromatics or isoparaffins—are catalyzed by sulfuric acid, hydrofluoric acid, BF_3 and $AlCl_3$.
2. Condensations of aldehydes and ketones are catalyzed homogeneously by acids and bases, but solid bases are preferred, such as anion exchange resins and alkali or alkaline earth hydroxides or phosphates.
3. Cracking, a rupturing of carbon-carbon bonds—for example, of gas oils to gasoline—is favored by silica-alumina, zeolites, and acid types generally. Zeolites have pores with small and narrow size distribution. They crack only molecules small enough to enter the pores. To restrain the undesirable formation of carbon and C_3-C_4 hydrocarbons, zeolite activity is reduced by dilution to 10 to 15 percent in silica-alumina.
4. Dehydration and dehydrogenation combined utilizes dehydration agents together with mild dehydrogenation agents. Included in this class are phosphoric acid, silica-magnesia, silica-alumina, alumina derived from aluminum chloride, and various metal oxides.
5. Esterification and etherification may be catalyzed by mineral acids or BF_3. The reaction of isobutylene with methanol to make MTBE is catalyzed by a sulfonated ion exchange resin.
6. Fischer-Tropsch oligomerization of $CO + H_2$ to make hydrocarbons and oxygenated compounds was originally catalyzed by cobalt, which forms the active carbonyl, but now iron promoted by potassium is favored. Dissociative chemisorption of CO has been observed in this process.
7. Halogenation and dehalogenation are catalyzed by substances that exist in more than one valence state and are able to donate and accept halogens freely. Silver and copper halides are used for gas-phase reactions, and ferric chloride commonly for liquid phase. Hydrochlorination (the absorption of HCl) is promoted by $BiCl_3$ or $SbCl_3$ and hydrofluorination by sodium fluoride or chromia catalysts that form fluorides under reaction conditions. Mercuric chloride promotes addition of HCl to acetylene to make vinyl chloride. Oxychlorination in the Stauffer process for vinyl chloride from ethylene is catalyzed by $CuCl_2$ with some KCl to retard its vaporization.
8. Hydration and dehydration employ catalysts that have a strong affinity for water. Alumina is the principal catalyst, but also used are aluminosilicates, metal salts and phosphoric acid or its metal salts on carriers, and cation exchange resins.
9. Hydrocracking is catalyzed by substances that promote cracking and hydrogenation together. In commercial use are Ni, Co, Cr, W, and V or their oxides, presulfided before use, on acid supports. Zeolites loaded with palladium also have been used.
10. Hydrodealkylation—for instance, of toluene to benzene—is catalyzed by supported oxides of Cr, Mo, and Co at 500 to 650°C and 50 atm.
11. Hydrodesulfurization. A commercial catalyst contains about 4 percent CoO and 12 percent MoO_3 on γ-alumina and is presulfided before use. Molybdena is a weak catalyst by itself and the cobalt has no catalytic action by itself.
12. Hydroformylation, or the OXO process, is the reaction of olefins with CO and H_2 to make aldehydes, which may subsequently be converted to higher alcohols. The catalyst base is cobalt naphthenate, which transforms to cobalt hydrocarbonyl in place. A rhodium complex that is more stable and functions at a lower temperature is also used.
13. Hydrogenation and dehydrogenation employ catalysts that form unstable surface hydrides. Raney nickel or cobalt are used for many reductions. In the hydrogenation of olefins, both olefin and hydrogen are chemisorbed, the latter with dissociation. Transition-group and bordering metals such as Fe, Ni, Co, and Pt are suitable, as well as transition-group oxides or sulfides. This class of reactions includes the important examples of ammonia and methanol syntheses, the Fischer-Tropsch, OXO, and SYNTHOL processes, and the production of alcohols, aldehydes, ketones, amines, and edible oils. In the sequence for making nylon, phenol is hydrogenated to cyclohexanol with nickel catalyst at 150°C (302°F) and 15 atm (221 psi); the product is hydrogenated to cyclohexanone at 400°C (752°F) using a zinc or copper catalyst; that product is hydrogenated to cyclohexane carboxylic acid at 150°C (302°F) and 15 atm (221 psi) with palladium on

charcoal; this last product is a precursor for ε-caprolactam, which goes on to make nylon.

14. Hydrolysis of esters is speeded up by both acids and bases. Soluble alkylaryl sulfonic acids or sulfonated ion exchange resins are suitable.

15. Isomerization is promoted by either acids or bases. Higher alkylbenzenes are isomerized in the presence of $AlCl_3$/HCl or BF_3/HF; olefins with most mineral acids, acid salts and silica-alumina; saturated hydrocarbons with $AlCl_3$ or $AlBr_3$ promoted by 0.1 percent of olefins.

16. Metathesis is the rupture and reformation of carbon-carbon bonds—for example, of propylene into ethylene plus butene. Catalysts are oxides, carbonyls, or sulfides of Mo, W, or Re.

17. Oxidation catalysts are either metals that chemisorb oxygen readily, such as platinum or silver, or transition metal oxides that are able to give and take oxygen by reason of their having several possible oxidation states. Ethylene oxide is formed with silver, ammonia is oxidized with platinum, and silver or copper in the form of metal screens catalyze the oxidation of methanol to formaldehyde. Cobalt catalysis is used in the following oxidations: butane to acetic acid and to butylhydroperoxide, cyclohexane to cyclohexylperoxide, acetaldehyde to acetic acid and toluene to benzoic acid. $PdCl_2$-$CuCl_2$ is used for many liquid-phase oxidations and V_2O_5 combinations for many vapor-phase oxidations.

18. Polymerization of olefins such as styrene is promoted by acid or base or sodium catalysts, and polyethylene is made with homogeneous peroxides. Condensation polymerization is catalyzed by acid-type catalysts such as metal oxides and sulfonic acids. Addition polymerization is used mainly for olefins, diolefins, and some carbonyl compounds. For these processes, initiators are coordination compounds such as Ziegler-type catalysts, of which halides of transition metals Ti, V, Mo, and W are important examples.

19. Reforming is the conversion primarily of naphthenes and alkanes to aromatics, but other reactions also occur under commercial conditions. Platinum or platinum/rhenium are the hydrogenation/dehydrogenation component of the catalyst and alumina is the acid component responsible for skeletal rearrangements.

20. Steam reforming is the reaction of steam with hydrocarbons to make town gas or hydrogen. The first stage is at 700 to 830°C (1,292 to 1,532°F) and 15–40 atm (221 to 588 psi). A representative catalyst composition contains 13 percent Ni supported on α-alumina with 0.3 percent potassium oxide to minimize carbon formation. The catalyst is poisoned by sulfur. A subsequent *shift reaction* converts CO to CO_2 and more H_2, at 190 to 260°C (374 to 500°F) with copper metal on a support of zinc oxide which protects the catalyst from poisoning by traces of sulfur.

Physical Characteristics With a few exceptions, solid catalysts are employed as porous pellets in a fixed or fluidized bed. Their physical characteristics of major importance are as follows.

• *Pellet size* is a major consideration. Shapes are primarily spherical, short cylindrical, or irregular. Special shapes like those used in mass-transfer equipment may be used to minimize pressure drop. In gas fluidized beds the diameters average less than 0.1 mm (0.0039 in); smaller sizes impose too severe loading on the entrainment recovery equipment. In slurry beds the diameters can be about 1.0 mm (0.039 in). In fixed beds the range is 2 to 5 mm (0.079 to 0.197 in). The competing factors are the pressure drop and accessibility of the internal surface, which vary in opposite directions with changes in diameter. With poor thermal conductivity, severe temperature gradients or peaks arise with large pellets that may lead to poor control of the reaction and undesirable side reactions like coking.

• *Specific surface* of solid spheres of 0.1 mm (0.0039 in) dia is 0.06 m^2/ml (18,300 ft^2/ft^3) and a porous activated alumina pellet has about 600 m^2/ml (1.83×10^8 ft^2/ft^3). Other considerations aside, a large surface is desirable because the rate of reaction is proportional to the accessible surface. On the other hand, large specific surface means pores of small diameter.

• *Pore diameter and distribution* are important factors. Small pores limit the accessibility of internal surface because of increased resistance to diffusion of reactants inwards. Diffusion of products outwards also is slowed, and degradation of those products may result. When the catalyst is expensive, the inaccessible internal surface is a liability, and in every case it makes for a larger reactor size. A more or less uniform pore diameter is desirable, but this is practically realizable only with molecular sieves. Those pellets that are extrudates of compacted masses of smaller particles have bimodal pore size distributions, between the particles and inside them. Micropores have diameters of 10 to 100 Å, macropores of 1,000 to 10,000 Å. The macropores provide rapid mass transfer into the interstices that lead to the micropores where the reaction takes place.

• *Diffusivity and tortuosity* affect resistance to diffusion caused by collision with other molecules (bulk diffusion) or by collision with the walls of the pore (Knudsen diffusion). Actual diffusivity in common porous catalysts is intermediate between the two types. Measurements and correlations of diffusivities of both types are known. Diffusion is expressed per unit cross section and unit thickness of the pellet. Diffusion rate through the pellet then depends on the porosity ϑ and a tortuosity factor τ that accounts for increased resistance of crooked and varied-diameter pores. Effective diffusion coefficient is $D_{\text{eff}} = D_{\text{theo}}\vartheta/\tau$. Empirical porosities range from 0.3 to 0.7, tortuosities from 2 to 7. In the absence of other information, Satterfield (*Heterogeneous Catalysis in Practice,* McGraw-Hill, 1991) recommends taking $\vartheta = 0.5$ and $\tau = 4$. In this area, clearly, precision is not a feature.

Rate of Reaction Rate equations of fluid reactions catalyzed by solids are of two main types:

1. Power law type, based directly on the law of mass action, say,

$$r_a = kP_a^{\alpha}P_b^{\beta}P_c^{\gamma}P_d^{\delta} \ldots \tag{23-59}$$

with a term for every reactant or product. The exponents are empirical and may be positive or negative, integral or fractional.

2. Hyperbolic, based on the Langmuir adsorption principle; for instance,

$$r_a = \frac{k(P_aP_b - P_cP_d/K_e)}{(1 + k_aP_a + K_bP_b + K_cP_c + K_dP_d)^2} \tag{23-60}$$

The latter kind of formulation is described at length in Sec. 7. The assumed mechanism is comprised of adsorption and desorption rates of the several participants and of the reaction rates of adsorbed species. In order to minimize the complexity of the resulting rate equation, one of the several rates in series may be assumed controlling. With several controlling steps the rate equation usually is not explicit but can be used with some extra effort.

Two quite successful rate equations of catalytic industrial processes are cited by Rase (*Chemical Reactor Design for Process Plants,* vol. 2, Wiley, 1977):

1. For the synthesis of ammonia,

$$r_{NH_3} = k(P_{N_2}P_{H_2}P_{NH_3}^{-1.5}\,P_{NH_3}P_{H_2}^{-1.5}) \tag{23-61}$$

2. For the oxidation of sulfur dioxide,

$$r_{SO_2} = \frac{k_1P_{SO_2}}{(P_{SO_3}^{0.5} + k_2P_{SO_2})^2}\left(P_{O_2} - \frac{P_{SO_3}}{K_eP_{SO_2}}\right)^2 \tag{23-62}$$

The first is a power law type modified for reversibility, and the second is a modified hyperbolic.

The partial pressures in the rate equations are those in the vicinity of the catalyst surface. In the presence of diffusional resistance, in the steady state the rate of diffusion through the stagnant film equals the rate of chemical reaction. For the reaction $A + B \Rightarrow C + \ldots$, with rate of diffusion of A limited,

$$r = r_d = r_s = k_1(P_{ag} - P_{as}) = \frac{k_2P_{as}P_b}{(1 + K_aP_{as} + P_b + K_cP_c + \cdots)^2} \tag{23-63}$$

The unknown partial pressure at the external surface can be eliminated as $P_{as} = P_{ag} - r/k_1$), which results in a cubic equation for r.

Another complication arises when not all of the internal surface of a porous catalyst is accessed. Then a factor called the effectiveness η is applied, making the power law equation, for instance,

$$r = k\eta P_a^{\alpha}P_b^{\beta}P_c^{\gamma}P_d^{\delta} \tag{23-64}$$

The effectiveness is known from experiment for important industrial catalysts and is correlated, in general, in terms of pore characteristics, concentrations, and specific rate equations.

From a statistical viewpoint, there is often little to choose between power law and hyperbolic equations as representations of data over an experimental range. The fact, however, that a particular hyperbolic equation is based on some kind of possible mechanism may lead to a belief that such an equation may be extrapolated more safely outside the experimental range, although there may be no guarantee that the controlling mechanism will remain the same in the extrapolated region.

Effectiveness As a reactant diffuses into a pore, it undergoes a falling concentration gradient and a falling rate of reaction. The concentration depends on the radial position in the pores of a spherical pellet according to

$$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = \frac{R_c}{D} \tag{23-65}$$

where R_C is the rate of reaction per unit volume; for a reaction of order n, $R_c = kC^n$. In terms of the normalized variables $f = C/C_s$ and $\rho = r/R$, and the Thiele modulus for a sphere,

$$\phi_s = R\sqrt{\frac{kC_s^{n-1}}{D}} \tag{23-66}$$

this becomes

$$\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho} = \phi_s^2 f^n \tag{23-67}$$

At the inlet to the pore, $\rho = 1$ and $f = f_s$. At the center, $\rho = 0$ and $df/d\rho = 0$.

Although the point values of the rate diminish with ρ, in the steady state the rate of reaction equals the rate of diffusion at the mouth of the pores. The effectiveness of the catalyst is a ratio

$$\eta = \frac{r_{\text{actual}}}{r_{\text{ideal}}} = \frac{D(dC/dr)_{r=R}}{\frac{4\pi R^3}{3}kC_s^n} \tag{23-68}$$

where r_{actual} = rate of diffusion at the mouth of the pore
r_{ideal} = rate on the assumption that all of the pore surface is exposed to the concentration at the external surface
C_s = concentration at the external surface

Numerical and some analytical solutions of the diffusion/reaction equations are represented closely by an empirical curve/fit,

$$\eta = \frac{1.0357 + 0.3173\phi_m + 0.000427\phi_m^2}{1 + 0.4172\phi_m + 0.1390\phi_m^2} \tag{23-69}$$

where the modified Thiele modulus for an nth order reaction, $R_c = kC^n$ per unit volume, is

$$\phi_m = 3\left(\frac{V_p}{A_p}\right)\left(\frac{3}{n+1}\right)^{1/2}\left(\frac{kC_s^{n-1}}{D_{\text{eff}}}\right)^{1/2} \tag{23-70}$$

where V_p/A_p = (volume of pellet)/(external surface of pellet)
= $R/3$ for spheres of radius R
= L for a slab with one permeable face
= $R/2$ for a cylinder with sealed flat ends

The analytical result for a first-order reaction in a spherical pellet is:

$$\eta = \frac{3}{\phi^2}\left(\frac{\phi}{\tanh\phi} - 1\right), \qquad \phi = R\sqrt{\frac{k}{D_{\text{eff}}}} \tag{23-71}$$

The effectiveness of a given size of pellet can be found experimentally by running tests of reaction conversion with a series of diminishing sizes of pellets until a limiting rate is found. Then η will be the ratio of the rate with the pellet size in question to the limiting value.

Since theoretical calculation of effectiveness is based on a hardly realistic model of a system of equal-sized cylindrical pores and a shaky assumption for the tortuosity factor, in some industrially important cases the effectiveness has been measured directly. For ammonia synthesis by Dyson and Simon (*Ind. Eng. Chem. Fundam.*, **7,** 605 [1968]) and for SO_2 oxidation by Kadlec et al. (*Coll. Czech. Chem. Commun.*, **33,** 2388, 2526 [1968]).

When account is taken of the effectiveness, the rate of reaction becomes

$$R_c = k\eta C_s^n$$

where η depends on C_s except for first-order reactions.

Example 5: Application of Effectiveness For a second-order reaction in a plug flow reactor the Thiele modulus is $\phi = 8\sqrt{C_s}$, and inlet concentration is $C_{s0} = 1.0$. The equation will be integrated for 80 percent conversion with Simpson's rule. Values of η are

$$(C_s, \eta) = (1.0, 0.272), (0.6, 0.338), (0.2, 0.510)$$

The material balance and the integral become

$$-V'dC_s = k\eta C_s^2 dV_r$$

$$kV_r/V' = \int_{0.2}^{1.0}\left(\frac{1}{\eta C_s^2}\right)dC = \left(\frac{0.4}{3}\right)[3.68 + 4\,(8.22) + 49.02] = 11.4$$

Adiabatic Reactions Aside from the Thiele modulus, two other parameters are necessary in this case:

$$\beta = -\frac{\Delta H_r DC_s}{\lambda T_s}$$

$$\gamma = \frac{E}{RT_s}$$

where ΔH_r = heat of reaction
λ = thermal conductivity
E = energy of activation
R = gas constant, 1.987 cal/g mol

Figure 23-19 is one of several by Weisz and Hicks (*Chem. Eng. Sci.*, **17,** 263 [1962]). Although this predicts some very large values of η in some ranges of the parameters, these values are mostly not realized in practice, as Table 23-5 shows. The modified Lewis number is $Lw' = \lambda_s/\rho_s C_{ps} D_{\text{eff}}$.

Deactivation in Process The active surface of a catalyst can be degraded by chemical, thermal, or mechanical factors. Poisons and

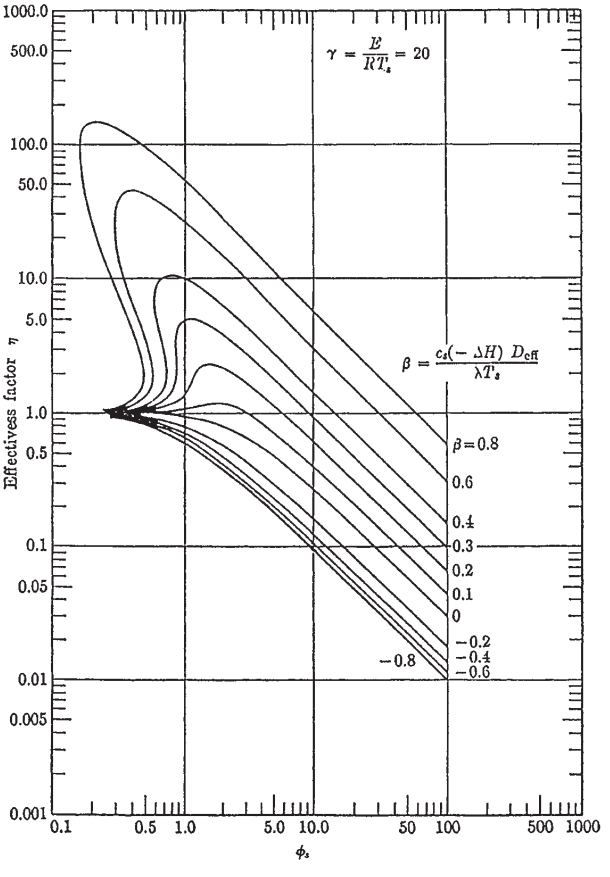


FIG. 23-19 Effectiveness of first-order reactions in spheres under adiabatic conditions (*Weisz and Hicks,* Chem. Eng. Sci., ***17,*** *265* [1962]).

TABLE 23-5 Parameters of Some Exothermic Catalytic Reactions

Reaction	β	γ	γβ	Lw'	ϕ
NH_3 synthesis	0.000061	29.4	0.0018	0.00026	1.2
Synthesis of higher alcohols from CO and H_2	0.00085	28.4	0.024	0.00020	—
Oxidation of CH_3OH to CH_2O	0.0109	16.0	0.175	0.0015	1.1
Synthesis of vinyl chloride from acetylene and HCl	0.25	6.5	1.65	0.1	0.27
Hydrogenation of ethylene	0.066	23–27	2.7–1	0.11	0.2–2.8
Oxidation of H_2	0.10	6.75–7.52	0.21–2.3	0.036	0.8–2.0
Oxidation of ethylene to ethylenoxide	0.13	13.4	1.76	0.065	0.08
Dissociation of N_2O	0.64	22.0	1.0–2.0	—	1–5
Hydrogenation of benzene	0.12	14–16	1.7–2.0	0.006	0.05–1.9
Oxidation of SO_2	0.012	14.8	0.175	0.0415	0.9

SOURCE: After Hlavacek, Kubicek, and Marek, *J. Catal.*, **15,** 17, 31 (1969).

inhibitors are known in specific cases. For instance, Thomas (*Catalytic Processes and Proven Catalysts,* Academic Press, 1970) often cites the poisons for the processes he describes. Potent poisons are compounds of P, S, As, Te, and Bi that have free electron pairs. In some cases a reduced life is simply accepted, as in the case of slow accumulation of trace metals from feed to catalytic cracking, but in other cases the deactivation is too rapid. Sulfur and water are removed from feed to ammonia synthesis, sulfur from the feed to platinum reforming, and arsenic from feed to SO_2 oxidation with platinum but not necessarily with vanadium. The catalyst also can be modified by additives; for instance, chromia to nickel to prevent sintering, rhenium to platinum to reduce coking, and so on. Reactivation sometimes is done in place; for instance, coke is burned off cracking catalyst or off nickel and nickel-molybdenum catalysts in a fluidized reactor/regenerator system. Platinum-alumina catalyst is regenerated in place by chlorine treatment. Much work has been done in this general field (Butt and Petersen, *Activation, Deactivation and Poisoning of Catalysts,* Academic Press, 1988). A list of 18 important industrial processes with catalyst lives and factors influencing them is in Delmon and Froment (*Catalyst Deactivation,* Elsevier, 1980). The lives range from a few days to several years.

Dependence of activity α may be simply on time onstream. One index is the ratio of the rate at time t to the rate with fresh catalyst,

$$\alpha = \frac{r_c \text{ @ } t}{r_c \text{ @ } t = 0} \tag{23-72}$$

The rate of destruction of active sites and pore structure can be expressed as a mass-transfer relation; for instance, as a second-order reaction

$$-\frac{d\alpha}{dt} = k_d \alpha^2 \tag{23-73}$$

and the corresponding integral

$$\alpha = \frac{1}{1 + k_d t} \tag{23-74}$$

The specific rate is expected to have an Arrhenius dependence on temperature. Deactivation by coke deposition in cracking processes apparently has this kind of correlation.

Assumption of a first-order rate law gives rise to

$$\alpha = \exp\,(k_1 - k_2 t) \tag{23-75}$$

Another relation that is sometimes successful is

$$\alpha = \frac{1}{1 + k_1 t^{k_2}} \tag{23-76}$$

When the feedstock contains constant proportions of reactive impurities, the rate of decline also may depend on the concentration of the main reactant, thus:

$$-\frac{d\alpha}{dt} = k_d\, \alpha^p\, C^q \tag{23-77}$$

Such a differential equation together with a rate equation for the main reactant constitutes a pair that must be solved simultaneously. Take the example of a CSTR for which the unsteady material balance is

$$C_0 = C + k\bar{t}\alpha C^q + \bar{t}\,\frac{dC}{dt} \tag{23-78}$$

With most values of the constants of these two equations a numerical solution will be needed.

The constants of the various time dependencies of activity are found by methods like those for finding constants of any rate equation, given suitable (α,t) data.

Uniform deactivation is one of the two limiting cases of the behavior of catalyst poisoning that are recognized. In one, the poison is distributed uniformly throughout the pellet and degrades it gradually. In the other, the poison is so effective that it kills completely as it enters the pore and is simultaneously removed from the stream. Complete deactivation begins at the mouth and moves gradually inward.

When uniform poisoning occurs the specific rate declines by a factor $1 - \beta$ where β is the fractional poisoning. Then a power law rate equation becomes

$$r_c = k_v(1 - \beta)\,\eta C_s^q \tag{23-79}$$

The effectiveness also depends on β through the Thiele modulus,

$$\phi = L\sqrt{\frac{k_v(1-\beta)C_s^{q-1}}{D}} \tag{23-80}$$

To find the effectiveness under poisoned conditions, this form of the modulus is substituted into the appropriate relation for effectiveness. For first-order reaction in slab geometry, for instance,

$$\eta = \frac{1}{L}\sqrt{\frac{D}{k_v(1-\beta)}}\tanh\left[L\sqrt{\frac{k_v(1-\beta)}{D}}\right] \tag{23-81}$$

Pore mouth (or shell) poisoning occurs when the poisoning of a pore surface begins at the mouth and moves gradually inward. In this case the reactant must diffuse through the dead zone before it starts to react. β is the fraction of the pore that is deactivated, C_1 is the concentration at the end of the inactive region, and $x = (1 - \beta)L$ is the coordinate there.

The rate of diffusion into the pore equals the rate of diffusion through the dead zone,

$$D\left(\frac{dC}{dx}\right)_{x=(1-\beta)L} = D\,\frac{\Delta C}{\Delta x} = d\,\frac{C_s - C_1}{\beta L} \tag{23-82}$$

The concentration profile in a porous slab is represented by

$$\frac{d^2C}{dx^2} = \frac{k}{D}\,C^q \tag{23-83}$$

At a sealed face or at the center of a slab with two permeable faces, the condition is:

$$\left(\frac{dC}{dx}\right)_{x=0} = 0 \tag{23-84}$$

The three preceding equations may be solved simultaneously by the shooting method. A result for a first-order reaction is shown in Fig. 23-20, together with the case of uniform poisoning.

Distribution of Catalyst in Pores Because of the practical requirements of manufacturing, commercial impregnated catalysts usually have a higher concentration of active ingredient near the outside than near the tip of the pores. This may not be harmful, because it seems that effectiveness sometimes is better with some kind of nonuniform distribution of a given mass of catalyst. Such effects may be present in cases where the rate exhibits a maximum as a function of

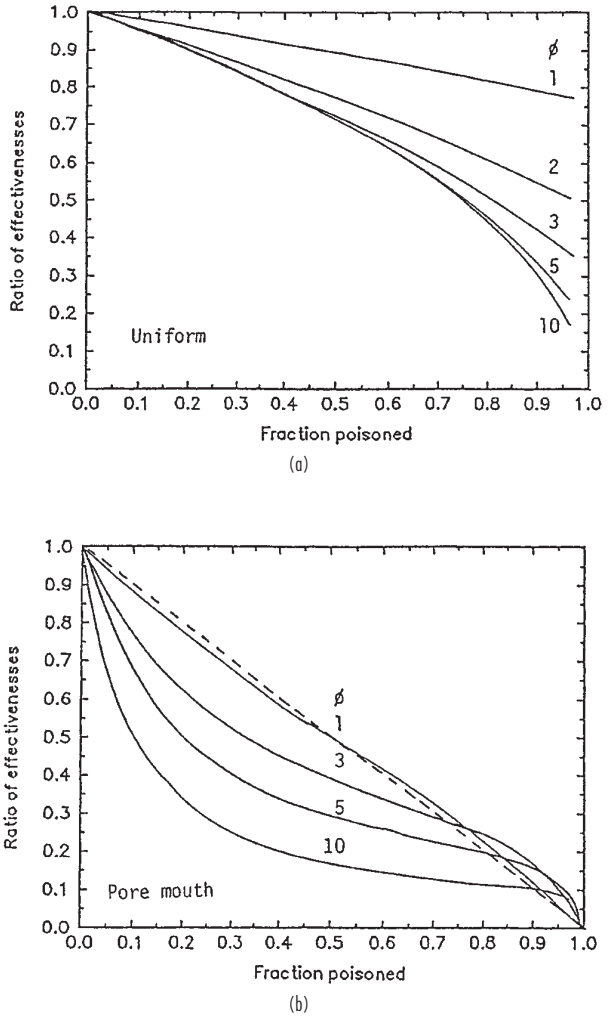


FIG. 23-20 Poisoning of a first-order reaction: (*a*) uniform poisoning, (*b*) pore mouth poisoning.

concentration of reactant, which is the case, for instance, with bimolecular Langmuir-Hinshelwood kinetics. Even under isothermal conditions, a catalyst's effectiveness can be several times unity at an optimum location of catalyst in the pore. Theoretical studies have recognized three zones: inner, middle, and outer (or egg yolk, egg white, and eggshell). Rather more theoretical studies have been made than experimental ones.

When a carrier is impregnated with a solution, where the catalyst deposits will depend on the rate of diffusion and the rate of adsorption on the carrier. Many studies have been made of Pt deposition from chloroplatinic acid (H_2PtCl_6) with a variety of acids and salts as coimpregnants. HCl results in uniform deposition of Pt. Citric or oxalic acid drive the Pt to the interior. HF coimpregnant produces an egg white profile. Photographs show such varied distributions in a single pellet.

Some studies of potential commercial significance have been made. For instance, deposition of catalyst some distance away from the pore mouth extends the catalyst's life when pore mouth deactivation occurs. Oxidation of CO in automobile exhausts is sensitive to the catalyst profile. For oxidation of propane the activity is eggshell > uniform > egg white. Nonuniform distributions have been found superior for hydrodemetallation of petroleum and hydrodesulfurization with molybdenum and cobalt sulfides. Whether any commercial processes with programmed pore distribution of catalysts are actually in use is not mentioned in the recent extensive review of Gavrillidis et al. (in Becker and Pereira, eds., *Computer-Aided Design of Catalysts*, Dekker, 1993, pp. 137–198), with the exception of monolithic automobile exhaust cleanup where the catalyst may be deposited some distance from the mouth of the pore and where perhaps a 25-percent longer life thereby may be attained.

Catalytic Membrane Reactors Membrane reactors combine reaction and separation in a single vessel. By removing one of the products of reaction, the membrane reactor can make conversion beyond thermodynamic equilibrium in the absence of separation.

For these studies, laboratory reactors have been of two main types: (1) a bed of catalyst pellets in series with a membrane, and (2) a membrane with catalyst deposited on the pore surface. Industrial membranes must be sturdy, temperature resistant, and affordable. Palladium alloys have high hydrogen permselectivity but are not commercially feasible because of their high cost. Microporous ceramic membranes in use thus far are able to separate gases only in accordance with the Knudsen diffusion law; that is, permeability is inversely proportional to the square root of the molecular weight. Efforts are being made for the development of membranes with molecular sieving properties, including zeolite, carbon, and polyphosphazene membranes.

Dehydrogenation processes in particular have been studied, with conversions in most cases well beyond thermodynamic equilibrium: Ethane to ethylene, propane to propylene, water-gas shift reaction $CO + H_2O \Leftrightarrow CO_2 + H_2$, ethylbenzene to styrene, cyclohexane to benzene, and others. Some hydrogenations and oxidations also show improvement in yields in the presence of catalytic membranes, although it is not obvious why the yields should be better since no separation is involved: hydrogenation of nitrobenzene to aniline, of cyclopentadiene to cyclopentene, of furfural to furfuryl alcohol, and so on; oxidation of ethylene to acetaldehyde, of methanol to formaldehyde, and so on.

At present, according to the review of Tsotsis et al. (in Becker and Pereira, eds., *Computer-Aided Design of Catalysts*, Dekker, 1993, pp. 471–551), there is no record of industrial implementation of reactors with catalytic membranes.

HOMOGENEOUS REACTIONS

Much of the basic theory of reaction kinetics presented in Sec. 7 of this Handbook deals with homogeneous reactions in batch and continuous equipment, and that material will not be repeated here. Material and energy balances and sizing procedures are developed for batch operations in ideal stirred tanks—during startup, continuation, and shutdown—and for continuous operation in ideal stirred tank batteries and plug flow tubulars and towers.

LIQUID PHASE

Batch reactions of single or miscible liquids are almost invariably done in stirred or pumparound tanks. The agitation is needed to mix multiple feeds at the start and to enhance heat exchange with cooling or heating media during the process.

Topics that acquire special importance on the industrial scale are the quality of mixing in tanks and the residence time distribution in vessels where plug flow may be the goal. The information about agitation in tanks described for gas/liquid and slurry reactions is largely applicable here. The relation between heat transfer and agitation also is discussed elsewhere in this Handbook. Residence time distribution is covered at length under "Reactor Efficiency." A special case is that of laminar and related flow distributions characteristic of non-Newtonian fluids, which often occurs in polymerization reactors.

Laminar Flow A mathematically simple deviation from uniform flow across a cross section is that of power law fluids whose linear velocity in a tube depends on the radial position $\beta = r/R$, according to the equation

$$u = \bar{u}\left(\frac{2n+1}{n+1}\right)(1-\beta^{(n+1)/n}) \tag{23-85}$$

where $\bar{u}$ is the average velocity. For normal fluids $n = 0$, for laminar ones $n = 1$, and other values apply to pseudoplastic and dilatant fluids. Along any particular radius, all molecules have the same residence time; that is, plug flow is achieved on that streamline. The average over the cross section is the value of primary interest.

For laminar flow, the velocity at the centerline is $u_0 = 2\bar{u}$. For a power law rate equation $r_c = kC^q$, the differential material balance on a streamline is

$$-u_0(1-\beta^2)dC = kC^q dL \tag{23-86}$$

when $q = 1$,

$$\frac{C}{C_0} = \exp(-kt) = \exp\left[\frac{kL}{u_0(1-\beta^2)}\right] \tag{23-87}$$

and when $q = 2$,

$$\frac{1}{C} - \frac{1}{C_0} = kt = \frac{kL}{u_0(1-\beta^2)} \tag{23-88}$$

The average concentration is found by integration over the cross section. After some algebraic manipulation, the result is

$$\frac{\bar{C}}{C_0} = 2t_0^2\int_{t_0}^{\infty} C\,\frac{dt}{t^3} \tag{23-89}$$

where $t_0 = 0.5\bar{t}$ is the residence time along the centerline and C is to be substituted from the previous equations. Figure 23-21 compares the performances of plug flow and laminar reactors of first- and second-order processes.

When it is deleterious, laminar flow can be avoided by mixing over the cross section. For this purpose static mixers in line can be provided. For very viscous materials and pastes, screws of the type used for pumping and extrusion are used as reactors.

Nonisothermal Operation Some degree of temperature control of a reaction may be necessary. Figures 23-1 and 23-2 show some of the ways that may be applicable to homogeneous liquids. More complex modes of temperature control employ internal surfaces, recycles, split flows, cold shots, and so on. Each of these, of course, requires an individual design effort.

Heat transfer through a vessel wall is often satisfactory:

1. In tubular reactors of only a few cm in diameter, the temperature is substantially uniform over the cross section so only an axial gradient occurs in the heat balance.
2. In towers with inert packing, both radial and axial gradients occur, although conduction in the axial direction often is neglected in view of the preponderant transfer of sensible enthalpy in a flow system.

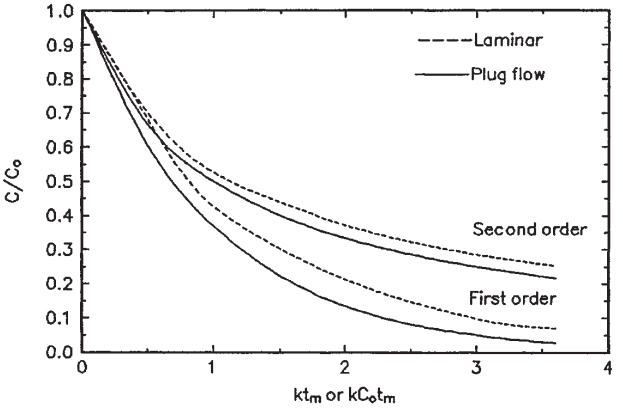


FIG. 23-21 Laminar compared with plug flow of first- and second-order reactions.

3. In an ideal CSTR, there are no gradients of temperature or composition, only the overall changes.

The simultaneous equations of heat and material balance and rate equations for these three cases are stated in several tables of Sec. 7.

The profiles of temperature and composition shown in Fig. 23-3 are not of homogeneous liquid reactions, but are perhaps representative of all kinds of reactions. Only in stirred tanks and some fluidized beds are nearly isothermal conditions practically attainable.

GAS PHASE

Although they are termed homogeneous, most industrial gas-phase reactions take place in contact with solids, either the vessel wall or particles as heat carriers or catalysts. With catalysts, mass diffusional resistances are present; with inert solids, the only complication is with heat transfer. A few of the reactions in Table 23-1 are gas-phase type, mostly catalytic. Usually a system of industrial interest is liquefied to take advantage of the higher rates of liquid reactions, or to utilize liquid homogeneous catalysts, or simply to keep equipment size down. In this section, some important noncatalytic gas reactions are described.

Mixing of feed gases and temperature control are major process requirements. Gases are usually mixed by injecting one of the streams from a high-speed nozzle into the rest of the gases, as in the flame reactor shown in Fig. 23-22*d*. Different modes of heat transfer are described, along with some processes that utilize each particular mode, following.

1. Heat is supplied from combustion gases through tubes in fired heaters. Olefins are made this way from light hydrocarbons and naphthas at 800°C (1472°F) and enough above atmospheric pressure to overcome friction. Superheated steam is injected to bring the final temperature up quickly and to retard carbon deposits. Contact times are 0.5 to 3.0 s, followed by rapid quenching. The total tube length of an industrial furnace may be more than 1,000 m. Other important gas-phase cracking processes are: Toluene ⇒ benzene, diphenyl ⇒ benzene, dicyclopentadiene ⇒ CPD, and butene-1 ⇒ butadiene. Figure 23-22*a* shows a cracking furnace.
2. Heat is transferred by direct contact with solids that have been preheated by combustion gases. The process is a cycle of alternate heating and reacting periods. The Wulf process for acetylene by pyrolysis of natural gas utilizes a heated brick checkerwork on a 4-min cycle of heating and reacting. The temperature play is 15°C (59°F), peak temperature is 1,200°C (2,192°F), residence time is 0.1 s of which 0.03 s is near the peak (Faith, Keyes, and Clark, *Industrial Chemicals*, vol. 27, Wiley, 1975).
3. The pebble heater recirculates refractory pebbles continuously through heating and reaction zones. The Wisconsin process for the fixation of nitrogen from air operates at 2,200°C (3,992°F), followed by extremely rapid quenching to freeze the small equilibrium content of nitrogen oxide that is made (Ermenc, *Chem. Eng. Prog.*, **52,** 149 [1956]). Such moving-bed units have been proposed for cracking to olefins but have been obsolesced like most moving-bed reactors.
4. The heat-carrying solids are particles of fluidized sand that circulate between the heating and reaction zones. The reaction section for light hydrocarbons is at 720 to 850°C (1,328 to 1,562°F), the regenerated sand returns at 50 to 100°C (122 to 212°F) above the reactor temperature. The heat comes mostly from the burning of carbon deposited on the sand. This equipment is perhaps competitively suited to cracking heavy stocks that coke readily.
5. Inert combustion gases are injected directly into the reacting stream in flame reactors. Figures 23-22*a* and 23-22*d* show two such devices used for making acetylene from light hydrocarbons and naphthas; Fig. 23-22*e* shows a temperature profile, reaction times in ms.
6. Burning a portion of a combustible reactant with a small additive of air or oxygen. Such oxidative pyrolysis of light hydrocarbons to acetylene is done in a special burner, at 0.001 to 0.01 s reaction time, peak at 1,400°C (2,552°F), followed by rapid quenching with oil or water.
7. Exothermic processes, with cooling through heat transfer surfaces or cold shots. In use are shell-and-tube reactors with small-diameter tubes, or towers with internal recirculation of gases, or multiple stages with intercooling. Chlorination of methane and other hydrocarbons results in a mixture of products whose relative amounts

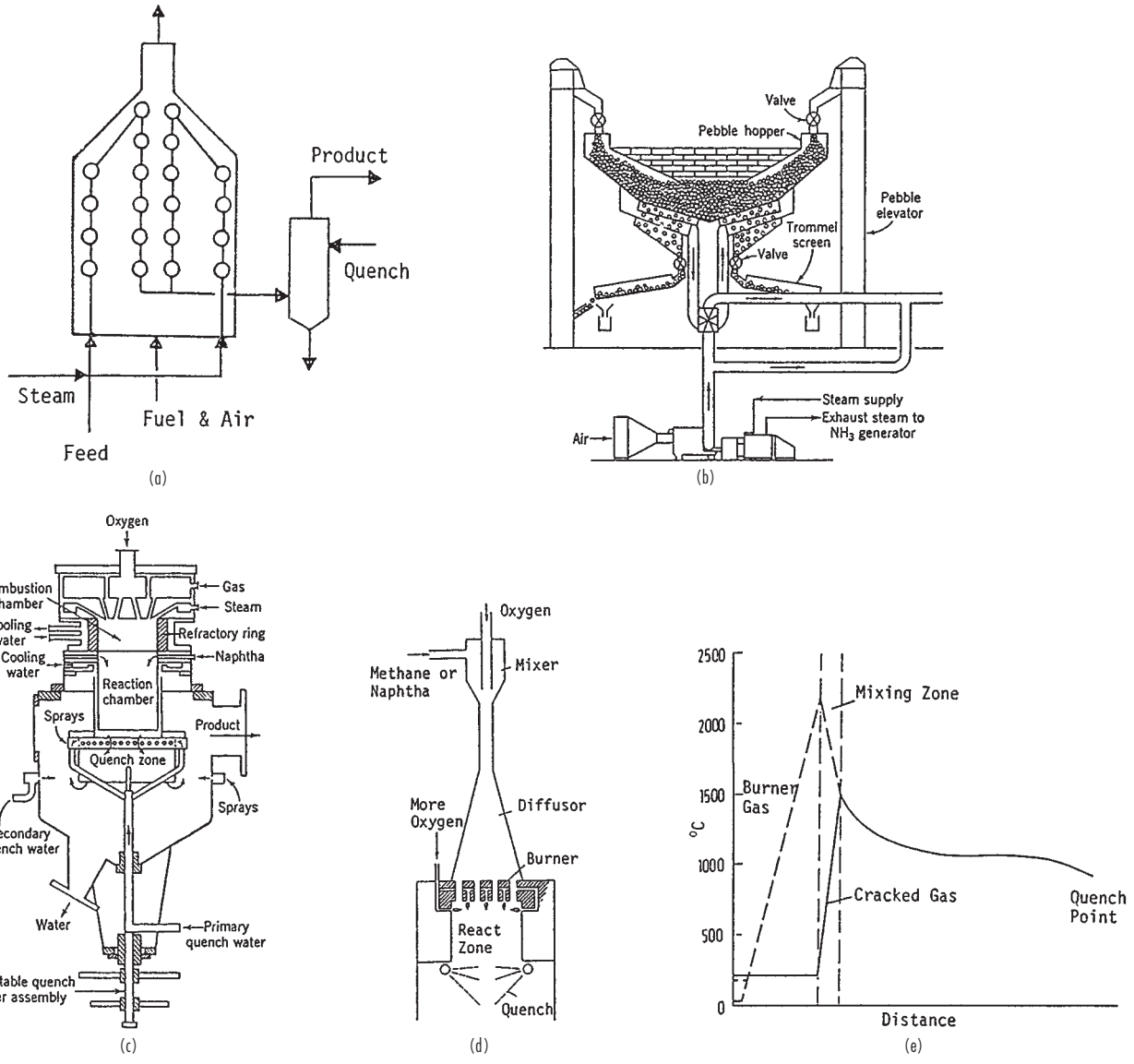


FIG. 23-22 Noncatalytic gas phase reactions. (*a*) Steam cracking of light hydrocarbons in a tubular fired heater. (*b*) Pebble heater for the fixation of nitrogen from air. (*c*) Flame reactor for the production of acetylene from hydrocarbon gases or naphthas (*Patton, Grubb, and Stephenson,* Pet. Ref. **37**(*11*), *180* [*1958*]). (*d*) Flame reactor for acetylene from light hydrocarbons (*BASF*). (*e*) Temperature profiles in a flame reactor for acetylene (Ullmann Encyclopadie der Technischen Chemie, *vol. 3, Verlag Chemie, 1973, p. 335*).

can be controlled by varying the Cl/HC ratio and recycling unwanted derivatives; for instance, recycling the mono and di derivatives when only the tri and tetra derivatives are of value, or keeping the chlorine ratio low when emphasizing the lower derivatives. Chlorination temperatures are normally kept in the range 230 to 400°C (446 to 752°F) to limit carbon formation, but may be raised to 500°C (932°F) when favoring CCl_4.

SUPERCRITICAL CONDITIONS

The critical properties of water are 374°C (705°F) and 218 atm (3,205 psi). Above this condition a heterogeneous mixture of water, organic compounds, and oxygen may become homogeneous. Then the rate of oxidation may be considerably accelerated because of (1) elimination of diffusional resistances, (2) increase of oxygen concentration by reason of greater density of the mixture, (3) enhanced solubility of oxygen and the organic compound, and (4) increase of the specific rate of reaction by pressure.

That the specific rate is affected by extremes of pressure—sometimes upward, sometimes downward—is well known. A review of this subject is by Kohnstam ("The Kinetic Effects of Pressure," in *Progress in Reaction Kinetics*, Pergamon, 1970). Three examples follow:

1. Thermal decomposition of Di-*t*-butyl peroxide in toluene at 120°C (248°F): 10^6k, 1/s, = 13.4 @ 1 atm (14.7 psi), = 5.7 @ 53 atm (779 psi)
2. Isomerization of cyclopropane at 491°C (916°F): 10^4k, 1/s, = 0.303 @ 0.067 atm (0.98 psi), = 1.30 @ 1.37 atm (20.1 psi), = 2.98 @ 84.1 atm (1,236 psi)
3. Fading of bromphenol blue at 25°C (77°F), 10^4k, L/m·s, = 9.3 @ 1 atm (14.7 psi), = 17.9 @ 1088 atm (16,000 psi)

Solubilities also may be changed greatly in the supercritical region. For naphthalene in ethylene at 35°C (95°F), the mol fraction of naphthalene goes from 0.004 @ 20 atm (294 psi) to 0.02 at 100 atm (1,470 psi) and 0.05 at 300 atm (4,410 psi).

High destructive efficiencies (above 99.99 percent) of complex organic compounds in water can be achieved with residence times under 5 min. Although there are some disagreements, the rate appears to be first order in the organic compound and first or zero order in oxygen.

Recent reviews of research in this area are: Bruno and Ely, eds., *Supercritical Fluid Technology,* CRC Press, 1991; Kiran and Brennecke, eds., *Supercritical Engineering Science,* ACS, 1992.

There is no mention in these reviews of any industrial implementation of supercritical kinetics. Two areas of interest are wastewater treatment—for instance, removal of phenol—and reduction of coking on catalysts by keeping heavy oil decomposition products in solution.

POLYMERIZATION

Polymers that form from the liquid phase may remain dissolved in the remaining monomer or solvent, or they may precipitate. Sometimes beads are formed and remain in suspension; sometimes emulsions form. In some processes solid polymers precipitate from a fluidized gas phase.

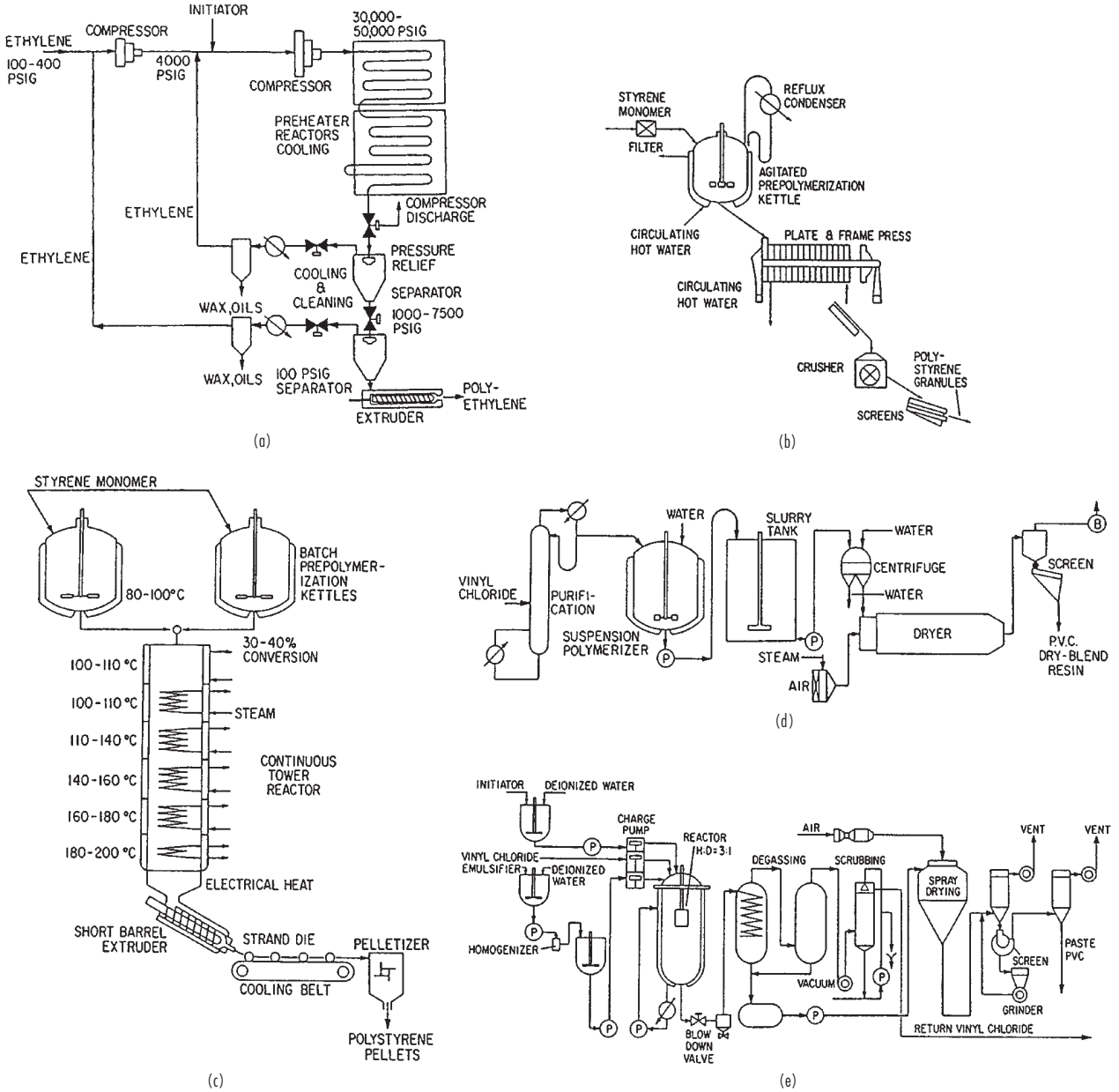


FIG. 23-23 Batch and continuous polymerizations. (*a*) Polyethylene in a tubular flow reactor, up to 2 km long by 6.4 cm ID. (*b*) Batch process for polystyrene. (*c*) Batch-continuous process for polystyrene. (*d*) Suspension (bead) process for polyvinylchloride. (*e*) Emulsion process for polyvinylchloride. (*Ray and Laurence, in Lapidus and Amundson,* eds., Chemical Reactor Theory Review, *Prentice-Hall, 1977.*)

Stirred batch and continuous reactors are widely used because of their flexibility, but a variety of reactor configurations are in use for particular cases. A selection may be made on rational grounds, or for historical reasons, or due simply to individual taste or a sense of proprietorship. For this complex area, in a given space, it is hardly possible to improve on the guide to selection of polymerization reactors by Gerrens (*German Chemical Engineering,* **4,** 1–13 [1981]; *ChemTech,* 380–383, 434–443 [1982]). Interested parties should go there. A general reference is Rodriguez (*Principles of Polymer Systems,* McGraw-Hill, 1989).

Polymerization processes are characterized by extremes. Industrial products are mixtures with molecular weights of 10^4 to 10^7. In a particular polymerization of styrene the viscosity increased by a factor of 10^6 as conversion went from 0 to 60 percent. The adiabatic reaction temperature for complete polymerization of ethylene is 1,800 K (3,240 R). Heat transfer coefficients in stirred tanks with high viscosities can be as low as 25 W/(m^2·°C) (16.2 Btu/[h·ft^2·°F]). Reaction times for butadiene-styrene rubbers are 8 to 12 h; polyethylene molecules continue to grow for 30 min; whereas ethyl acrylate in 20% emulsion reacts in less than 1 min, so monomer must be added gradually to keep the temperature within limits. Initiators of the chain reactions have concentration of 10^{-8} g mol/L so they are highly sensitive to poisons and impurities.

The physical properties of polymers depend largely on the molecular weight distribution, which can cover a wide range. Since it is impractical to fractionate the products and reformulate them into desirable ranges of molecular weights, immediate attainment of desired properties must be achieved through the correct choice of reactor type and operating conditions, notably of distributions of residence time and temperature. Those factors are influenced by high viscosities. In tubular reactors there are strong gradients in the radial direction. In stirred tanks ideal mixing is not attainable; wide variations in temperatures may result, and stagnant zones and bypassing may exist. Devices that counteract these unfavorable characteristics include inserts that cause radial mixing, scraping impellers, screw feeders, hollow-shaft impellers with coolant flow through them, recirculation through draft tubes, and so on. High viscosities of bulk and melt polymerizations are avoided with solution, bead, or emulsion operations. Then more nearly normal RTDs exist in CSTR batteries and tubular flow vessels.

KINDS OF POLYMERIZATION PROCESSES

Bulk Polymerization The monomer and initiators are reacted without or with mixing; without mixing to make useful shapes directly, like bakelite products. Because of viscosity limitations, stirred bulk polymerization is not carried to completion but only to 30 to 60 percent or so, with the remaining monomer stripped out and recycled. A variety of processes is in use for polystyrene, two of which are represented in Figs. 23-23*b* and 23-23*c*. A twin-screw extruder is used for polymerization of trioxane and of polyamide.

Bead Polymerization Bulk reaction proceeds in independent droplets of 10 to 1,000 μm diameter suspended in water or other medium and insulated from each other by some colloid. A typical suspending agent is polyvinyl alcohol dissolved in water. The polymerization can be done to high conversion. Temperature control is easy because of the moderating thermal effect of the water and its low viscosity. The suspensions sometimes are unstable and agitation may be critical. Only batch reactors appear to be in industrial use: polyvinyl acetate in methanol, copolymers of acrylates and methacrylates, polyacrylonitrile in aqueous $ZnCl_2$ solution, and others. Bead polymerization of styrene takes 8 to 12 h.

Emulsions Emulsions have particles of 0.05 to 5.0 μm diameter. The product is a stable latex, rather than a filterable suspension. Some latexes are usable directly, as in paints, or they may be coagulated by various means to produce massive polymers. Figures 23-23*d* and 23-23*e* show bead and emulsion processes for vinyl chloride. Continuous emulsion polymerization of butadiene-styrene rubber is done in a CSTR battery with a residence time of 8 to 12 h. Batch treating of emulsions also is widely used.

Solution Polymerization These processes may retain the polymer in solution or precipitate it. Polyethylene is made in a tubular flow reactor at supercritical conditions so the polymer stays in solution. In the Phillips process, however, after about 22 percent conversion when the desirable properties have been attained, the polymer is recovered and the monomer is flashed off and recyled (Fig. 23-23*a*). In another process, a solution of ethylene in a saturated hydrocarbon is passed over a chromia-alumina catalyst, then the solvent is separated and recyled. Another example of precipitation polymerization is the copolymerization of styrene and acrylonitrile in methanol. Also, an aqueous solution of acrylonitrile makes a precipitate of polyacrylonitrile on heating to 80°C (176°F).

A factor in addition to the RTD and temperature distribution that affects the molecular weight distribution (MWD) is the nature of the chemical reaction. If the period during which the molecule is growing is short compared with the residence time in the reactor, the MWD in a batch reactor is broader than in a CSTR. This situation holds for many free radical and ionic polymerization processes where the reaction intermediates are very short lived. In cases where the growth period is the same as the residence time in the reactor, the MWD is narrower in batch than in CSTR. Polymerizations that have no termination step—for instance, polycondensations—are of this type. This topic is treated by Denbigh (*J. Applied Chem.,* **1,** 227 [1951]).

FLUIDS AND SOLID CATALYSTS

In the design of reactors for fluids in the presence of granular catalysts, account must be taken of heat transfer, pressure drop and contacting of the phases, and, in many cases, of provision for periodic or continuous regeneration of deteriorated catalyst. Several different kinds of vessel configurations for continuous processing are in commercial use. Some reactors with solid catalysts are represented in Figs. 23-18 and 23-24.

Most solid catalytic processes employ fixed beds. Although fluidized beds have the merit of nearly uniform temperature and can be designed for continuous regeneration, they cost more and are more difficult to operate, require extensive provisions for dust recovery, and suffer from backmixing. Accordingly, they have been adopted on a large scale for only a few processes. Ways have been found in some instances to avoid the need for continuous regeneration. In the case of platinum reforming with fixed beds, for instance, a large recycle of hydrogen prevents coke deposition while a high temperature compensates for the retarding effect of hydrogen on this essentially dehydrogenating process.

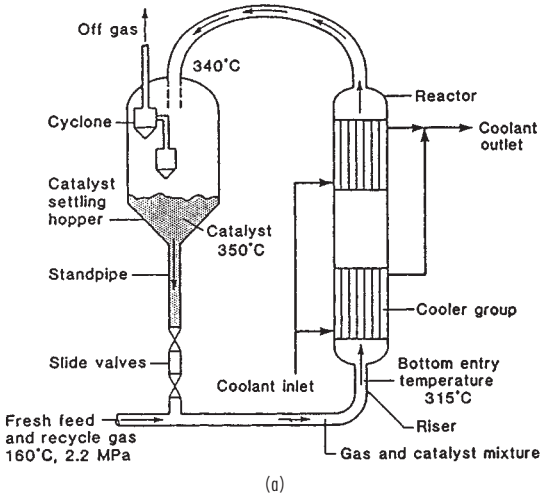
SINGLE FIXED BEDS

These are used for adiabatic processing or when it is practical to embed heat-transfer surface in the bed. Usually, heat transfer is more effective with the catalyst inside small tubes than outside them. Hydrodesulfurization of petroleum fractions is one large-scale application of single-bed reactors.

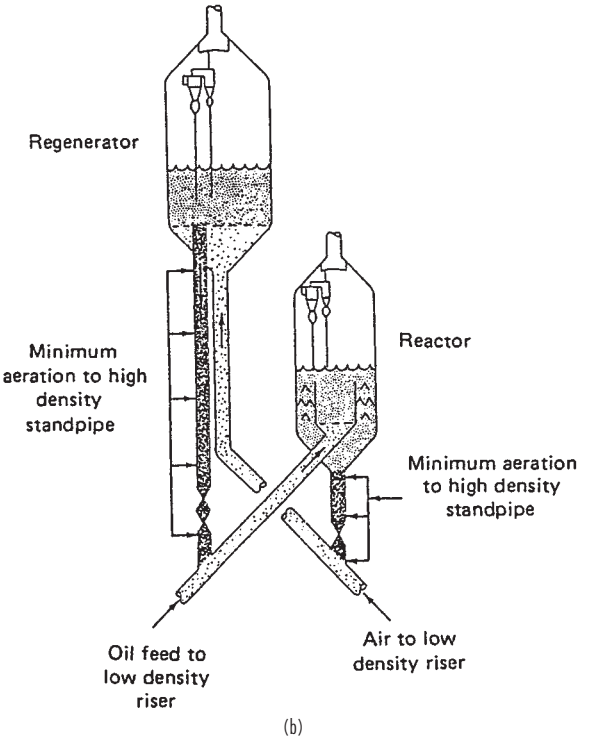
During filling, the catalyst is distributed uniformly to avoid the possibility of channeling that could lead to poor heat transfer, poor conversion, and harm to the catalyst because of hot spots. During startup, sudden surges of flow may disturb the bed and are to be avoided. For instance, in a study of a hydrodesulfurizer by Murphree et al. (*Ind. Eng. Chem. Proc. Des. & Dev.,* **3,** 381 [1964]) the efficiency of conversion in a commercial size unit varied between 47 and 80 percent with different modes of loading and startup.

MULTIPLE FIXED BEDS

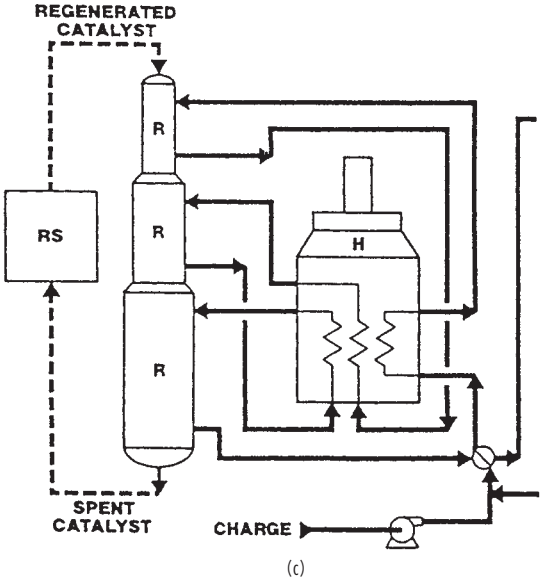
These enable temperature control with built-in exchangers between the beds or with pumparound exchangers. Converters for ammonia, SO_3, cumene, and other processes may employ as many as five or six beds in series. The Sohio process for vapor-phase oxidation of propylene to acrylic acid uses two beds of bismuth molybdate at 20 to 30 atm (294 to 441 psi) and 290 to 400°C (554 to 752°F). Oxidation of ethylene to ethylene oxide also is done in two stages with supported



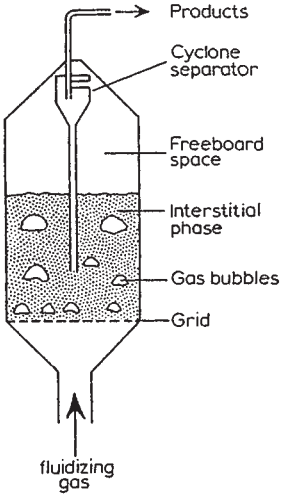
(a)



(b)



(c)



(d)

FIG. 23-24 Reactors with moving catalysts. (*a*) Transport fluidized type for the Sasol Fischer-Tropsch process, nonregenerating. (*b*) Esso type of stable fluidized bed reactor/regenerator for cracking petroleum oils. (*c*) UOP reformer with moving bed of platinum catalyst and continuous regeneration of a controlled quantity of catalyst. (*d*) Flow distribution in a fluidized bed; the catalyst rains through the bubbles.

silver catalyst, the first stage to 30 percent conversion, the second to 76 percent, with a total of 1.0 s contact time.

MULTITUBULAR REACTORS

These reactors are of shell-and-tube configuration and mostly have the catalyst in the tubes, although some ammonia converters have the catalyst on the shell side. Hundreds of tubes of a few cm diameter may be required. Their diameters may be approximately 8 times the diameters of the pellets and lengths limited by allowable pressure drop. Catalyst pellet sizes usually are in the range of 0.3 to 0.5 cm (0.76 to 1.27 in). Uniform loading is ensured by using special equipment that charges the same amount of catalyst to each tube at a definite rate. After filling, each tube is checked for pressure drop.

Maleic anhydride is made by oxidation of benzene with air above 350°C (662°F) with V-Mo catalyst in a multitubular reactor with 2-cm tubes. The heat-transfer medium is a eutectic of molten salt at 375°C (707°F). Even with small tubes, the heat transfer is so limited that a peak temperature 100°C (212°F) above the shell side is developed and moves along the tubes.

Butanol by the hydrogenation of crotonaldehyde is made in a reactor with 4,000 tubes, 28 mm (0.029 ft) ID by 10.7 m (35.1 ft) long (Berty, in Leach, ed., *Applied Industrial Catalysis,* vol. 1, Academic Press, 1983, p. 51).

Vinyl acetate is made from ethylene, oxygen, and acetic acid in the vapor phase at 150 to 175°C (302 to 347°F) with supported Pd catalyst in packed tubes, 25 mm (0.082 ft) ID.

Vinyl chloride is made from ethylene and chlorine with Cu and K chlorides. The Stauffer process employs 3 multitubular reactors in series with 25 mm (0.082 ft) ID tubes (Naworski and Velez, in Leach, ed., *Applied Industrial Catalysis,* vol. 1, Academic Press, 1983, p. 251).

SLURRY REACTORS

These reactors for liquids and liquids plus gases employ small particles in the range of 0.05 to 1.0 mm (0.0020 to 0.039 in), the minimum size limited by filterability. Small diameters are used to provide as large an interface as possible since the internal surface of porous pellets is poorly accessible to the liquid phase. Solids concentrations up to 10 percent by volume can be handled. In hydrogenation of oils with Ni catalyst, however, the solids content is about 0.5 percent, and in the manufacture of hydroxylamine phosphate with Pd-C it is 0.05 percent. Fischer-Tropsch slurry reactors have been tested with concentrations of 10 to 950 g catalyst/L (0.624 to 59.3 lbm/ft^3) (Satterfield and Huff, *Chem. Eng. Sci.,* **35,** 195 [1980]).

Advantages of slurry reactors are high heat capacity, which makes for good temperature stability, and good heat transfer. Catalyst activity can be maintained by partial removal of degraded material and replenishment during operation. Disadvantages are a lower conversion for a given size because of essentially complete backmixing, power for agitation to keep the catalyst in suspension and to enhance heat transfer, and separation of entrained catalyst from the product.

Most industrial processes with slurry reactors are used for gases with liquids, such as chlorination, hydrogenation, and oxidation.

Liquid benzene is chlorinated in the presence of metallic iron turnings or Raschig rings at 40 to 60°C (104 to 140°F). Carbon tetrachloride is made from CS_2 by bubbling chlorine into it in the presence of iron powder at 30°C (86°F).

Substances that have been hydrogenated in slurry reactors include: nitrobenzene with Pd-C, butynediol with Pd-$CaCO_3$, chlorobenzene with Pt-C, toluene with Raney Ni, and acetone with Raney Ni.

Some oxidations in slurry reactors include: cumene with metal oxides, cyclohexene with metal oxides, phenol with CuO, and *n*-propanol with Pt.

TRANSPORT (OR ENTRAINMENT) REACTORS

The fluid and catalyst travel through the vessel in essentially plug flow and are separated downstream by settling and with cyclones and filters. The main publicized applications are for cracking to gasoline-range hydrocarbons with highly active zeolite catalysts and in the Sasol Fischer-Tropsch process. A considerable body of experience with transport of solids by entrainment with gases (pneumatic conveying) and with pneumatic drying has been accumulated; nevertheless, five years elapsed before the Sasol reactor was made to function satisfactorily. A principal advantage of transport reactors is that they approach plug flow, whereas stable fluidized beds have much backmixing. Figure 23-24*a* shows an in-line heat exchanger in the Sasol unit. The catalyst is promoted iron. It circulates through the 1.0-m (3.28-ft) ID riser at 72,600 kg/h (160,000 lbm/h) at 340°C (644°F) and 23 atm (338 psi) and has a life of about 50 days.

FLUIDIZED BEDS

Particle sizes in fluidized bed applications average below 0.1 mm, but very small particles impose severe restrictions on the recovery of entrained material. The original reactor of this type was the Winkler coal gasifier (patented 1922), followed in 1940 by the Esso cracker, several hundred of which have been operated; they are now being replaced by riser reactors with zeolite catalysts. The other large application is combustion of solid fuels, for which some 30 installations are listed in *Encyclopedia of Chemical Technology,* vol. 10, Wiley, 1980, p. 550). A list of 55 other applications with references is in the same source. It is not clear how many of these are successful because many processes were tried with enthusiasm for the new technology and found wanting.

Advantages of fluidized beds are temperature uniformity, good heat transfer, and transportability of rapidly decaying catalyst between reacting and regenerating sections. Disadvantages are attrition, recovery of fines, and backmixing. Baffles have been used to reduce backmixing.

Phthalic anhydride is made by oxidation of naphthalene at temperatures of 340 to 380°C (644 to 716°F) controlled by heat exchangers immersed in the bed. At these temperatures the catalyst is stable and need not be regenerated. The excellence of temperature control was a major factor for the adoption of this process, but it was obsolesced by 1972.

Acrylonitrile, on the other hand, is still being made from propylene, ammonia, and oxygen at 400 to 510°C (752 to 950°F) in this kind of equipment. The good temperature control with embedded heat exchangers permits catalyst life of several years.

Another process where good temperature control is essential is the synthesis of vinyl chloride by chlorination of ethylene at 200 to 300°C (392 to 572°F), 2 to 10 atm (29.4 to 147 psi), with supported cupric chloride, but a process with multitubular fixed beds is a strong competitor.

Although it is not a catalytic process, the roasting of iron sulfide in fluidized beds at 650 to 1,100°C (1,202 to 2,012°F) is analogous. The pellets are 10-mm (0.39-in) diameter. There are numerous plants, but they are threatened with obsolescence because cheaper sources of sulfur are available for making sulfuric acid.

MOVING BEDS

The catalyst, in the form of large granules, circulates by gravity and gas lift between reaction and regeneration zones. The first successful operation was the Houdry cracker that replaced a plant with fixed beds that operated on a 10-min cycle between reaction and regeneration. It was soon obsolesced by FCC units. The only currently publicized moving bed process is a UOP platinum reformer (Fig. 23-24*c*) that regenerates a controlled quantity of catalyst on a continuous basis. It is not known how competitive this process is with units having multiple reactors that regenerate in place or operate at such low severity that catalyst life of several years is obtained.

THIN BEDS AND WIRE GAUZES

Fast catalytic reactions that must be quenched rapidly are done in contact with wire screens or thin layers of fine granules. Ammonia in a 10% concentration in air is oxidized by flow through a fine gauze catalyst made of 2 to 10% Rh in Pt, 10 to 30 layers, 0.075-mm (0.0030-in) diameter wire. Contact time is 0.0003 s at 750°C (1,382°F) and 7 atm (103 psi) followed by rapid quenching. Methanol is oxidized to formaldehyde in a thin layer of finely divided silver or a multilayer screen, with a contact time of 0.01 s at 450 to 600°C (842 to 1,112°F).

GAS/LIQUID REACTIONS

Industrial gas/liquid reaction processes are of four main categories:

1. Gas purification or the removal of relatively small amounts of impurities such as CO_2, CO, COS, SO_2, H_2S, NO, and others from air, natural gas, hydrogen for ammonia synthesis, and others
2. Liquid phase processes, such as hydrogenation, halogenation, oxidation, nitration, alkylation, and so on
3. Manufacture of pure products, such as sulfuric acid, nitric acid, nitrates, phosphates, adipic acid, and so on
4. Biochemical processes, such as fermentation, oxidation of sludges, production of proteins, biochemical oxidations, and so on

Reaction between an absorbed solute and a reagent reduces the equilibrium partial pressure of the solute, thus increasing the rate of mass transfer. The mass-transfer coefficient likewise is enhanced, which contributes further to increased absorption rates. Extensive theoretical analyses of these effects have been made, but rather less experimental work and design guidelines.

For reaction between a gas and a liquid, three modes of contacting are possible: (1) the gas is dispersed as bubbles in the liquid, (2) the liquid is dispersed as droplets in the gas, and (3) the liquid and gas are brought together as thin films over a packing or wall. The choice between these modes is an important problem. Some considerations are the magnitude and distribution of the residence times of the phases, the power requirements, the scale of the operation, the opportunity for heat transfer, and so on. Industrial equipment featuring particular factors is available. The main types of apparatus appear in Fig. 23-25, but many variations are practiced. Specific liquid/gas processes are represented in Fig. 23-26. Equipment is selected and designed by a combination of theory, pilot plant work, and experience, with rather less reliance on theory than in some other areas of reactor design.

MASS TRANSFER COEFFICIENTS

The resistance to transfer of mass between a gas and a liquid is assumed confined to that of fluid films between the phases. Let

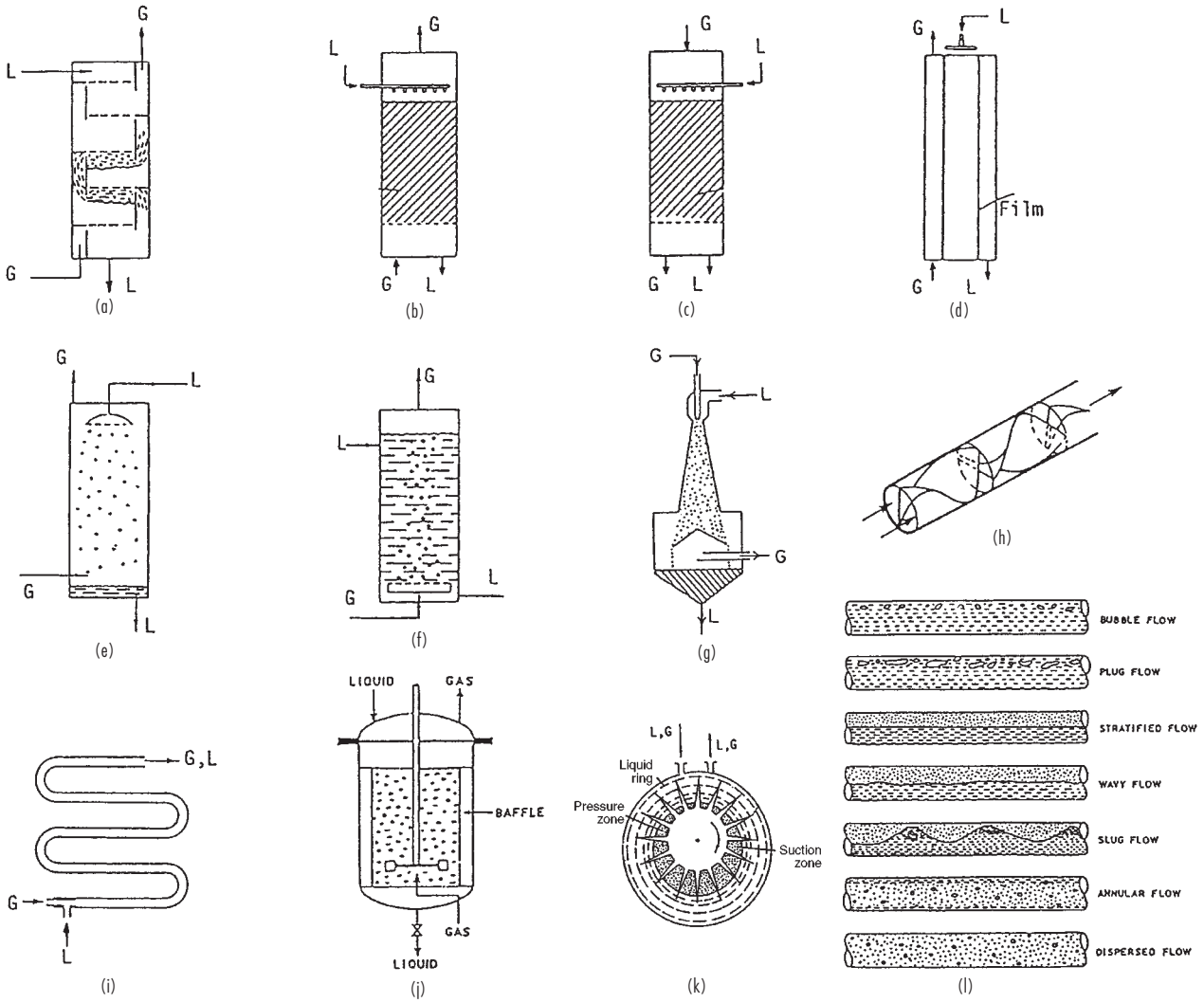


FIG. 23-25 Types of industrial gas/liquid reactors. (*a*) Tray tower. (*b*) Packed, counter current. (*c*) Packed, parallel current. (*d*) Falling liquid film. (*e*) Spray tower. (*f*) Bubble tower. (*g*) Venturi mixer. (*h*) Static in line mixer. (*i*) Tubular flow. (*j*) Stirred tank. (*k*) Centrifugal pump. (*l*) Two-phase flow in horizontal tubes.

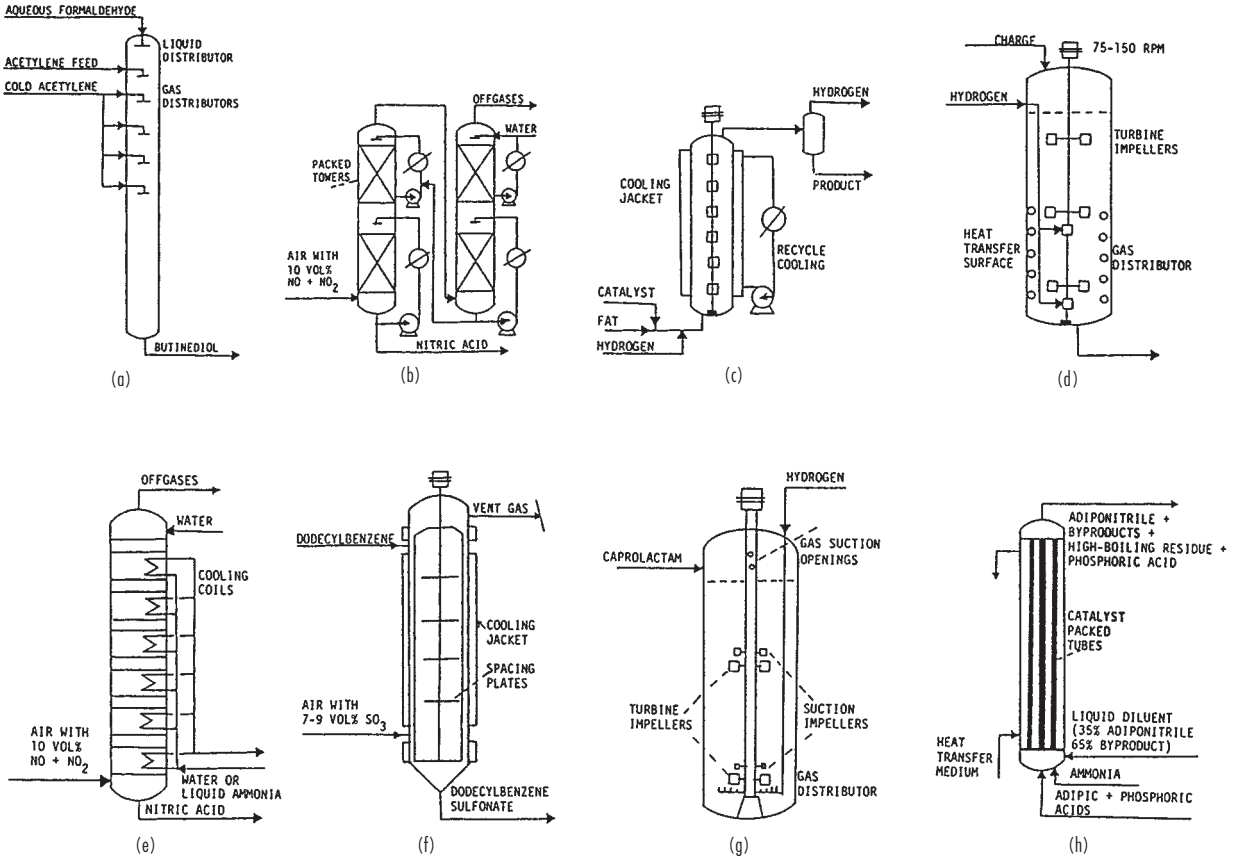


FIG. 23-26 Examples of reactors for specific liquid/gas processes. (*a*) Trickle reactor for synthesis of butinediol, 1.5 m diameter by 18 m high. (*b*) Nitrogen oxide absorption in packed columns. (*c*) Continuous hydrogenation of fats. (*d*) Stirred tank reactor for batch hydrogenation of fats. (*e*) Nitrogen oxide absorption in a plate column. (*f*) A thin-film reactor for making dodecylbenzene sulfonate with SO_3. (*g*) Stirred tank reactor for the hydrogenation of caprolactam. (*h*) Tubular reactor for making adiponitrile from adipic acid in the presence of phosphoric acid.

D = diffusivity

$p_i = f(C_i)$ or $p_i = HC_i$, equilibrium relation at the interface

a = interfacial area/unit volume

z_g, z_L = film thicknesses

The steady rates of solute transfer are

$$r = k_g a(p_g - p_i)$$
$$= k_L a(C_i - C_L)$$

where

$$k_g = \frac{D}{z_g}$$

$$k_L = \frac{D}{z_L}$$

are the mass-transfer coefficients of the individual films. Overall coefficients are defined by

$$r = K_g a(p_g - p_L) = K_L a(C_g - C_L)$$

Upon introducing the equilibrium relation $p = HC$, the relation between the various mass-transfer coefficients is

$$\frac{1}{K_g a} = \frac{H}{K_L a} = \frac{1}{k_g a} + \frac{H}{k_L a} \qquad (23\text{-}90)$$

When the solubility is low, H is large and $k_L \Rightarrow K_L$; when the solubility is high, H is small and $k_g \Rightarrow K_g$.

For purely physical absorption, the mass-transfer coefficients depend on the hydrodynamics and the physical properties of the phases. Many correlations exist; for example, that of Dwivedi and Upadhyay (*Ind. Eng. Chem. Proc. Des. & Dev.*, **16,** 157 [1977]),

$$k = \frac{u'}{\mathrm{Sc}^{2/3}}\left(\frac{0.765}{\mathrm{Re}^{0.82}} + \frac{0.365}{\mathrm{Re}^{0.386}}\right) \qquad (23\text{-}91)$$

where $\mathrm{Re} = \rho u' d_p/\mu$.

With a reactive solvent, the mass-transfer coefficient may be enhanced by a factor E so that, for instance, K_g is replaced by EK_g. Like specific rates of ordinary chemical reactions, such enhancements must be found experimentally. There are no generalized correlations. Some calculations have been made for idealized situations, such as complete reaction in the liquid film. Tables 23-6 and 23-7 show a few spot data. On that basis, a tower for absorption of SO_2 with NaOH is smaller than that with pure water by a factor of roughly 0.317/7.0 = 0.045. Table 23-8 lists the main factors that are needed for mathematical representation of $K_g a$ in a typical case of the absorption of CO_2 by aqueous monethanolamine. Figure 23-27 shows some of the complex behaviors of equilibria and mass-transfer coefficients for the absorption of CO_2 in solutions of potassium carbonate. Other than Henry's law, $p = HC$, which holds for some fairly dilute solutions, there is no general form of equilibrium relation. A typically complex equation is that for CO_2 in contact with sodium carbonate solutions (Harte, Baker, and Purcell, *Ind. Eng. Chem.*, **25,** 528 [1933]), which is

$$p_{CO_2} = \frac{137 f^2 N^{1.29}}{S(1-f)(365 - T)}, \quad \text{Torr} \qquad (23\text{-}92)$$

TABLE 23-6 Typical Values of $K_G a$ for Absorption in Towers Packed with 1.5-in Intalox Saddles at 25% Completion of Reaction*

Absorbed gas	Absorbent	$K_G a$, lb mol/(h·ft³·atm)
Cl_2	H_2O·NaOH	20.0
HCl	H_2O	16.0
NH_3	H_2O	13.0
H_2S	H_2O·MEA	8.0
SO_2	H_2O·NaOH	7.0
H_2S	H_2O·DEA	5.0
CO_2	H_2O·KOH	3.10
CO_2	H_2O·MEA	2.50
CO_2	H_2O·NaOH	2.25
H_2S	H_2O	0.400
SO_2	H_2O	0.317
Cl_2	H_2O	0.138
CO_2	H_2O	0.072
O_2	H_2O	0.0072

*To convert in to cm, multiply by 2.54; lb mol/(h·ft³·atm) to kg mol/(h·m³·kPa), multiply by 0.1581.

SOURCE: From Eckert, et al., *Ind. Eng. Chem.,* **59,** 41 (1967).

TABLE 23-7 Selected Absorption Coefficients for CO_2 in Various Solvents in Towers Packed with Raschig Rings*

Solvent	$K_g a$, lb mol/(h·ft³·atm)
Water	0.05
1-*N* sodium carbonate, 20% Na as bicarbonate	0.03
3-*N* diethanolamine, 50% converted to carbonate	0.4
2-*N* sodium hydroxide, 15% Na as carbonate	2.3
2-*N* potassium hydroxide, 15% K as carbonate	3.8
Hypothetical perfect solvent having no liquid-phase resistance and having infinite chemical reactivity	24.0

*Basis: L = 2,500 lb/(h·ft²); G = 300 lb/(h·ft²); T = 77°F; pressure, 1.0 atm. To convert lb mol/(h·ft³·atm) to kg mol/(h·m³·kPa) multiply by 0.1581.

SOURCE: From Sherwood, Pigford, and Wilke, *Mass Transfer,* McGraw-Hill, 1975, p. 305.

TABLE 23-8 Correlation of $K_G a$ for Absorption of CO_2 by Aqueous Solutions of Monoethanolamine in Packed Towers*

$$K_G a = F\left(\frac{L}{\mu}\right)^{2/3}[1 + 5.7(C_e - C)M\, e^{0.0067T - 3.4p}]$$

where $K_G a$ = overall gas-film coefficient, lb mol/(h·ft³·atm)
μ = viscosity, centipoises
C = concentration of CO_2 in the solution, mol/mol monoethanolamine
M = amine concentration of solution (molarity, g mol/L)
T = temperature, °F
p = partial pressure, atm
L = liquid-flow rate, lb/(h·ft²)
C_e = equilibrium concentration of CO_2 in solution, mol/mol monoethanolamine
F = factor to correct for size and type of packing

Packing	F	Basis for calculation of F
5- to 6-mm glass rings	7.1×10^{-3}	Shneerson and Leibush data, 1-in column, atmospheric pressure
⅜-in ceramic rings	3.0×10^{-3}	Unpublished data for 4-in column, atmospheric pressure
¾- by 2-in polyethylene Tellerettes	3.0×10^{-3}	Teller and Ford data, 8-in column, atmospheric pressure
1-in steel rings		
1-in ceramic saddles	2.1×10^{-3}	
1½- and 2-in ceramic rings	$0.4–0.6 \times 10^{-3}$	Gregory and Scharmann and unpublished data for two commercial plants, pressures 30 to 300 psig

*To convert in to cm multiply by 2.54.

SOURCE: From Kohl and Riesenfeld, *Gas Purification,* Gulf, 1985.

where f = fraction of total base present as bicarbonate
N = normality, 0.5 to 2.0
S = solubility of CO_2 in pure water at 1 atm, g mol/L
T = temperature, 65 to 150°F

COUNTERCURRENT ABSORPTION TOWERS

Consider mass transfer in a countercurrent tower, packed or spray or bubble. Let

$$G_m = \frac{\text{mol inert gas}}{(\text{unit time})(\text{unit cross section})}$$

$$L_m = \frac{\text{mol solute-free liquid}}{(\text{unit time})(\text{unit cross section})}$$

$$Y = \frac{y}{(1-y)} = \frac{\text{mol solute, gas phase}}{\text{mol inert gas, vapor phase}}$$

$$X = \frac{x}{(1-x)} = \frac{\text{mol solute in the liquid}}{\text{mol inert solvent in the liquid}}$$

Z = height of active tower section.

The material balance over a differential height is

$$G_m dY = L_m dX$$

In terms of gas film conditions,

$$G_m dY = k_g a(p_g - p_i)dZ$$

The partial pressure of the gas is related to the total pressure π by

$$p_g = y\pi = \frac{Y}{1+Y}\pi, \qquad p_i = \frac{Y_i}{1+Y_i}\pi$$

Substitution and rearrangement leads to the equation for the tower height,

$$Z = \frac{G_m}{\pi}\int_{Y_2}^{Y_1} \frac{(1+Y)(1+Y_i)}{k_g a(Y - Y_i)}\,dY \tag{23-93}$$

Similarly, in terms of the liquid-phase condition,

$$C = \frac{X}{1+X}C_t$$

$$C_t = \frac{\text{mol (solute + solvent)}}{\text{volume of liquid}}$$

$$L_m dX = k_L a(C_i - C)dZ$$

$$Z = \frac{L_m}{C_t}\int_{x_2}^{x_1} \frac{(1+X)(1+X_i)}{k_L a(X_i - X)}\,dX \tag{23-94}$$

The balance around one end of the tower can be written:

$$X = X_1 + \frac{G_m}{L_m}(Y - Y_1) \tag{23-95}$$

If the equilibrium relation is

$$y_i = mx \qquad \text{or} \qquad \frac{Y_i}{1+Y_i} = m\frac{X}{1+X} \tag{23-96}$$

or any other functional form, substitution of Eqs. (23-95) and (23-96) into (23-93) will enable the last equation to be solved numerically. Graphical methods of solution are explained in the chapter on physical absorption.

For physical absorption, values of the mass-transfer coefficients may not vary greatly, so a mean value could be adequate and could be taken outside the integral sign, but for reactive absorption the variation usually is too great.

Note that the tower height is inversely proportional to the enhanced mass-transfer coefficient, or to the enhancement factor itself.

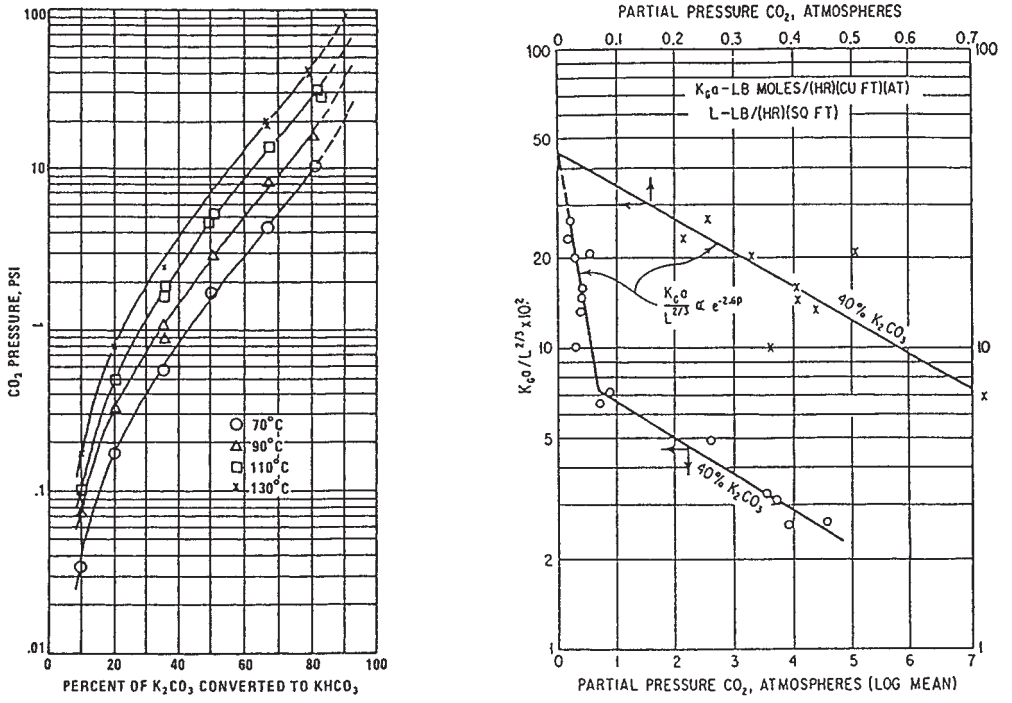


FIG. 23-27 CO_2 in potassium carbonate solutions: (*a*) equilibrium in 20% solution, (*b*) mass-transfer coefficients in 40% solutions. (*Data cited by Kohl and Riesenfeld,* Gas Purification, *Gulf Publishing, 1985.*)

FIRST-ORDER OR PSEUDO-FIRST-ORDER REACTION IN A LIQUID FILM

A reactant A diffuses into a stagnant liquid film where the concentration of excess reactant B remains essentially constant at C_{b0}. At the inlet face the concentration is C_{ai}. Making the material balance over a differential dz of the distance leads to the second-order diffusional equation,

$$\frac{d^2C_a}{dz^2} = \frac{k_c C_{b0}}{D} C_a = \alpha^2 C_a$$

The boundary conditions are $C_a = C_{ai}$ where $z = 0$, and $C_a = C_{aL}$ where $z = z_L$. The integral is

$$C_a = \frac{C_{aL} \sinh(\alpha z) + C_{ai} \sinh[\alpha(z_L - z)]}{\sinh(\alpha z_L)}$$

Since this is a steady condition, the rate of reaction in the film equals the rate of input to the film,

$$r = -D\left(\frac{dC_a}{dz}\right)_{C_a = C_{ai}} = \frac{\alpha D[\cosh(\alpha z_L) + C_{aL}]}{\sinh(\alpha z_L)} \qquad (23\text{-}97)$$

An important special case is that of complete reaction in the film; that is, for $C_{aL} = 0$ where $z = z_L$. Then,

$$r = \alpha D \coth(\alpha z_L)(C_{ai} - 0)$$
$$= \alpha z_L \left(\frac{D}{z_L}\right) \coth(\alpha z_L)(C_{ai} - 0)$$
$$= k_L \beta \coth(\beta)\, \Delta C_a = k_L E\, \Delta C_a \qquad (23\text{-}98)$$

where the enhancement factor is

$$E = \beta \coth(\beta)$$

and a parameter called the *Hatta number* is

$$\beta = \alpha z_L = z_L \sqrt{\frac{k_c C_{b0}}{D}} = \frac{\sqrt{k_c D C_{b0}}}{k_L} \qquad (23\text{-}99)$$

Note that this parameter has the same form as the Thiele number which occurs in the theory of diffusion/reaction in catalyst pores.

SECOND-ORDER REACTION IN A LIQUID FILM

A pure gas A diffuses into a liquid film where it reacts with B from the liquid phase. Material balances on the two participants are:

$$D_a \frac{d^2C_a}{dz^2} = k_c C_a C_b \qquad (23\text{-}100)$$

$$D_b \frac{d^2C_b}{dz^2} = k_c C_a C_b \qquad (23\text{-}101)$$

At the gas/liquid interface, $z = 0$, $C_a = C_{ai}$, $dC_b/dz = 0$. On the liquid side of the film, $z = z_L$, $C_b = C_{bL}$. The volume of the bulk liquid per unit of interfacial area

$$V_L = \text{total volume} - \text{film volume}$$
$$= \frac{\varepsilon}{a - z_L} \qquad (23\text{-}102)$$

where ε is fractional holdup of liquid and a is interfacial area per unit volume of liquid. The remaining boundary condition at z_L is

$$-D_a\left(\frac{dC_a}{dz}\right) = k_c C_{aL} C_{bL}\left(\frac{\varepsilon}{a - z_L}\right) \qquad (23\text{-}103)$$

The numerical solution of these equations is shown in Fig. 23-28. This is a plot of the enhancement factor E against the Hatta number, with several other parameters. The factor E represents an enhancement of the rate of transfer of A caused by the reaction compared with physical absorption with zero concentration of A in the liquid. The uppermost line on the upper right represents the pseudo-first-order reaction, for which $E = \beta \coth \beta$.

Three regions are identified with different requirements of ε and a, and for which particular kinds of contacting equipment may be best:

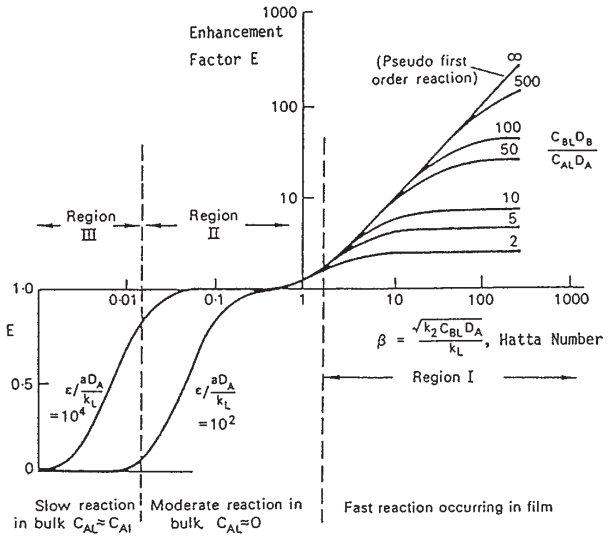


FIG. 23-28 Enhancement factor E and Hatta number of first- and second-order gas/liquid reactions, numerical solutions by several hands.

$$\text{Hatta number} = \beta = \frac{\sqrt{k_2 C_{B2} D_A}}{k_L}$$

(*Coulson and Richardson,* Chemical Engineering, *vol. 3, Pergamon, 1971, p. 80.*)

Region I, $\beta > 2$. Reaction is fast and occurs mainly in the liquid film so $C_{aL} \Rightarrow 0$. The rate of reaction $r_a = k_L a E C_{ai}$ will be large when a is large, but liquid holdup is not important. Packed towers or stirred tanks will be suitable.

Region II, $0.02 < \beta < 2$. Most of the reaction occurs in the bulk of the liquid. Both interfacial area and holdup of liquid should be high. Stirred tanks or bubble columns will be suitable.

Region III, $\beta < 0.02$. Reaction is slow and occurs in the bulk liquid. Interfacial area and liquid holdup should be high, especially the latter. Bubble columns will be suitable.

SCALE-UP FROM LABORATORY DATA

Three criteria for scale-up are that the laboratory and industrial units have the same mass-transfer coefficients k_L and Ek_L and the same ratio of the specific interfacial surface and liquid holdup a/ε_L. Tables 23-9 and 23-10 give order-of-magnitude values of some parameters that may be expected in common types of liquid/gas contactors.

Auxiliary data are the sizes of bubbles and droplets. These data and the holdups of the two phases are measured by a variety of standard techniques. Interfacial area measurements utilize techniques of transmission or reflection of light. Data on and methods for finding solubilities of gases or the relation between partial pressure and concentration in liquid are also well established.

Hatta Number A film-conversion parameter is defined as

$$M = \frac{\text{maximum possible conversion in the film}}{\text{maximum diffusional transport through the film}} = \frac{k_c C_a C_{b0} z_L}{Da(C_a - 0)/z_L} = \frac{k_c C_{b0} z_L^2}{D_a} = \frac{D_a k_c C_{b0}}{k_L^2} = \overset{2}{\text{Ha}} \qquad (23\text{-}104)$$

When $\overset{2}{\text{Ha}} >> 1$, all of the reaction occurs in the film and the amount of interfacial area is controlling, necessitating equipment that has a large interfacial area. When $\overset{2}{\text{Ha}} << 1$, no reaction occurs in the film and the bulk volume controls. The Hatta criteria are often applied in the following form.

Ha < 0.3	Reaction needs large bulk liquid volume
0.3 < Ha < 3.0	Reaction needs large interfacial area and large bulk liquid volume
Ha > 3.0	Reaction needs large interfacial area

Of the parameters making up the Hatta number, liquid diffusivity data and measurement methods are well reviewed in the literature.

Specific Rate k_c For the liquid-phase reaction without the complications of diffusional resistances, the specific rate can be determined after dissolving the gas solute and liquid reactant separately in the same solvent, mixing the two liquids quickly and thoroughly and following the progress of the liquid-phase reaction at the elevated pressure. Unless the reaction is very fast, the mixing time may be ignored. There may be an advantage in employing supercritical conditions at which gas solubility may be appreciably enhanced.

A number of successful devices have been in use for finding mass-transfer coefficients, some of which are sketched in Fig. 23-29, and all of which have known or adjustable interfacial areas. Such laboratory testing is reviewed, for example, by Danckwerts (*Gas-Liquid Reactions,* McGraw-Hill, 1970) and Charpentier (in Ginetto and Silveston, eds., *Multiphase Chemical Reactor Theory, Design, Scaleup,* Hemisphere, 1986).

Gas-Film Coefficient k_g Since the gas film is not affected by the liquid-phase reaction, one of the many available correlations for physical absorption may be applicable. The coefficient also may be found directly after elimination of the liquid-film coefficient by employing a solution that reacts instantaneously and irreversibly with the dissolved gas, thus canceling out any backpressure. Examples of such systems are SO_2 in NaOH and NH_3 in H_2SO_4.

Liquid-Film Coefficients k_L (Physical) and Ek_L (Reactive) The gas-side resistance can be eliminated by employing a pure gas, thus leaving the liquid film as the only resistance. Alternatively, after the gas-film resistance has been found experimentally or from corre-

TABLE 23-9 Mass-Transfer Coefficients, Interfacial Areas and Liquid Holdup in Gas/Liquid Reactions

Type of reactor	ε_L, %	k_G, gm mol/(cm²·s·atm) s·atm) × 10⁴	k_L cm/s × 10²	a, cm²/cm³ reactor	$k_L a$, s⁻¹ × 10²
Packed columns					
Countercurrent	2–25	0.03–2	0.4–2	0.1–3.5	0.04–7
Cocurrent	2–95	0.1–3	0.4–6	0.1–17	0.04–102
Plate columns					
Bubble cap	10–95	0.5–2	1–5	1–4	1–20
Sieve plates	10–95	0.5–6	1–20	1–2	1–40
Bubble columns	60–98	0.5–2	1–4	0.5–6	0.5–24
Packed bubble columns	60–98	0.5–2	1–4	0.5–3	0.5–12
Tube reactors					
Horizontal and coiled	5–95	0.5–4	1–10	0.5–7	0.5–70
Vertical	5–95	0.5–8	2–5	1–20	2–100
Spray columns	2–20	0.5–2	0.7–1.5	0.1–1	0.07–1.5
Mechanically agitated bubble reactors	20–95	—	0.3–4	1–20	0.3–80
Submerged and plunging jet	94–99	—	0.15–0.5	0.2–1.2	0.03–0.6
Hydrocyclone	70–93	—	10–30	0.2–0.5	2–15
Ejector reactor	—	—	—	1–20	—
Venturi	5–30	2–10	5–10	1.6–25	8–25

SOURCE: From Charpentier, *Advances In Chemical Engineering,* vol. 11, Academic Press, 1981, pp. 2–135).

TABLE 23-10 Order-of-Magnitude Data of Equipment for Contacting Gases and Liquids

Device	k_La, s^{-1}	V, m^3	k_LaV, m^3/s (duty)	a, m^{-1}	ε_L	Liquid mixing	Gas mixing	Power per unit volume, kW/m^3
Baffled agitated tank	0.02–0.2	0.002–100	10^{-4}–20	~200	0.9	~Backmixed	Intermediate	0.5–10
Bubble column	0.05–0.01	0.002–300	10^{-5}–3	~20	0.95	~Plug	Plug	0.01–1
Packed tower	0.005–0.02	0.005–300	10^{-5}–6	~200	0.05	Plug	~Plug	0.01–0.2
Plate tower	0.01–0.05	0.005–300	10^{-5}–15	~150	0.15	Intermediate	~Plug	0.01–0.2
Static mixer (bubble flow)	0.1–2	Up to 10	1–20	~1000	0.5	~Plug	Plug	10–500

SOURCE: From J. C. Middleton, in Harnby, Edwards, and Nienow, *Mixing in the Process Industries,* Butterworth, 1985.

lations, the liquid-film coefficient can be calculated from a measured overall liquid-film coefficient with the relation

$$\frac{1}{K_L} = \frac{1}{Hk_g} + \frac{1}{k_L} \tag{23-105}$$

In order to allow integration of countercurrent relations like Eq. (23-93), point values of the mass-transfer coefficients and equilibrium data are needed, over ranges of partial pressure and liquid-phase compositions. The same data are needed for the design of stirred tank performance. Then the conditions vary with time instead of position. Because of limited solubility, gas/liquid reactions in stirred tanks usually are operated in semibatch fashion, with the liquid phase charged at once, then the gas phase introduced gradually over a period of time. CSTR operation rarely is feasible with such systems.

INDUSTRIAL GAS/LIQUID REACTION PROCESSES

Two lists of gas/liquid reactions of industrial importance have been compiled recently. The literature survey by Danckwerts (*Gas-Liquid Reactions,* McGraw-Hill, 1970) cites 40 different systems. A supplementary list by Doraiswamy and Sharma (*Heterogeneous Reactions: Fluid-Fluid-Solid Reactions,* Wiley, 1984) cites another 50 items, and indicates the most suitable kind of reactor to be used for each. Estimates of values of parameters that may be expected of some types of gas/liquid reactors are in Tables 23-9 and 23-10.

Examples are given of common operations such as absorption of ammonia to make fertilizers and of carbon dioxide to make soda ash. Also of recovery of phosphine from offgases of phosphorous plants; recovery of HF; oxidation, halogenation, and hydrogenation of various organics; hydration of olefins to alcohols; oxo reaction for higher aldehydes and alcohols; ozonolysis of oleic acid; absorption of carbon monoxide to make sodium formate; alkylation of acetic acid with isobutylene to make *tert*-butyl acetate, absorption of olefins to make various products; HCl and HBr plus higher alcohols to make alkyl halides; and so on.

By far the greatest number of installations is for the removal or recovery of mostly small concentrations of acidic and other components from air, hydrocarbons, and hydrogen. Hundreds of such plants are in operation, many of them of great size. They mostly employ either packed or tray towers. Power requirements for such equipment are small. When the presence of solid impurities could clog the equipment or when the pressure drop must be low, spray towers are used in spite of their much larger size for a given capacity and scrubbing efficiency.

Removal of CO_2 and H_2S from Inert Gases, Packed and Tray Towers The principal reactive solvents for the removal of acidic constituents from gas streams are aqueous solutions of monethanolamine (MEA), diethanolamine (DEA) and K_2CO_3. These are all regenerable. Absorption proceeds at a lower temperature or higher pressure and regeneration in a subsequent vessel at higher temperature or lower pressure, usually with some assistance from stripping steam. CO_2 is discharged to the atmosphere or recovered to make dry ice. H_2S is treated for recovery of the sulfur. Any COS in the offgases is destroyed by catalytic hydrogenation.

Some performance data of plants with DEA are shown in Table 23-11. Both the absorbers and strippers have trays or packing. Vessel diameters and allowable gas and liquid flow rates are established by the same correlations as for physical absorptions. The calculation of tower heights utilizes data of equilibria and enhanced mass-transfer coefficients like those of Fig. 23-27 but for DEA solutions. Such calculations are complex enough to warrant the use of the professional methods of tower design that are available from a number of service companies.

Partly because of their low cost, aqueous solutions of sodium or potassium carbonate also are used for CO_2 and H_2S. Potassium bicarbonate has the higher solubility so the potassium salt is preferred. In view of the many competitive amine and carbonate plants that are in operation, fairly close figuring apparently is required to find an economic superiority, but other intangibles may be involved.

Both the equilibria and the enhancement of the coefficients can be improved by additives, of which sodium arsenite is the major one in use, but sodium hypochlorite and small amounts of amines also are effective. *Sterically hindered amines* as promoters are claimed by Say et al. (*Chem. Eng. Prog.,* **80**(10), 72–77 [1984]) to result in 50 percent more capacity than ordinary amine promoters of carbonate solutions.

Many operating data for carbonate plants are cited by Kohl and Riesenfeld (*Gas Purification,* Gulf, 1985) but not including tower heights. Pilot plant tests, however, are reported on 0.10- and 0.15-m (4- and 6-in) columns packed to depths of 9.14 m (30 ft) of Raschig rings by Benson et al. (*Chem. Eng. Prog.,* **50,** 356 [1954]).

Sulfur Dioxide, Spray Towers Flue gases and offgases from sulfuric acid plants contain less than 0.5 percent SO_2; smelter gases like those from ore processing plants may contain 8 percent. The high-concentration streams are suitable for the manufacture of sulfuric acid. The low concentrations usually are regarded as contaminants to be destroyed or recovered as elemental sulfur by, for example, the Claus process.

Of the removal processes that have attained commercial status, the current favorite employs a slurry of lime or limestone. The activity of the reagent is promoted by the addition of small amounts of carboxylic acids such as adipic acid. The gas and the slurry are contacted in a spray tower. The calcium salt is discarded. A process that employs aqueous sodium citrate, however, is suited for the recovery of elemental sulfur. The citrate solution is regenerated and recycled. (Kohl and Riesenfeld, *Gas Purification,* Gulf, 1985, p. 356.)

Limestone is pulverized to 80 to 90 percent through 200 mesh. Slurry concentrations of 5 to 40% have been checked in pilot plants. Liquid to gas ratios are 0.2 to 0.3 gal/MSCF. Flue gas enters at 149°C (300°F) at a velocity of 2.44 m/s (8 ft/s). Utilization of 80 percent of the solid reagent may be approached. Flow is in parallel downward. Residence times are 10 to 12 s. At the outlet the particles are made just dry enough to keep from sticking to the wall, and the gas is within 11 to 28°C (20 to 50°F) of saturation. The fine powder is recovered with fabric filters.

Rotary wheel atomizers require 0.8 to 1.0 kWh/1,000 L. The lateral throw of a spray wheel requires a large diameter to prevent accumulation on the wall; length to diameter ratios of 0.5 to 1.0 are in use in such cases. The downward throw of spray nozzles permits smaller diameters but greater depths; *L/D* ratios of 4 to 5 or more are used. Spray vessel diameters of 15 m (50 ft) or more are known. The technology of spray drying is applicable.

In one test facility, a gas with 4,000 ppm SO_2 had 95 percent removal with lime and 75 percent removal with limestone.

Stirred Vessels Gases may be dispersed in liquids by spargers or nozzles and redispersed by packing or trays. More intensive dispersion and redispersion is obtained by mechanical agitation. At the same time, the agitation will improve heat transfer and will keep catalyst particles in suspension if necessary. Power inputs of 0.6 to 2.0 kW/m^3 (3.05 to 10.15 hp/1,000 gal) are suitable.

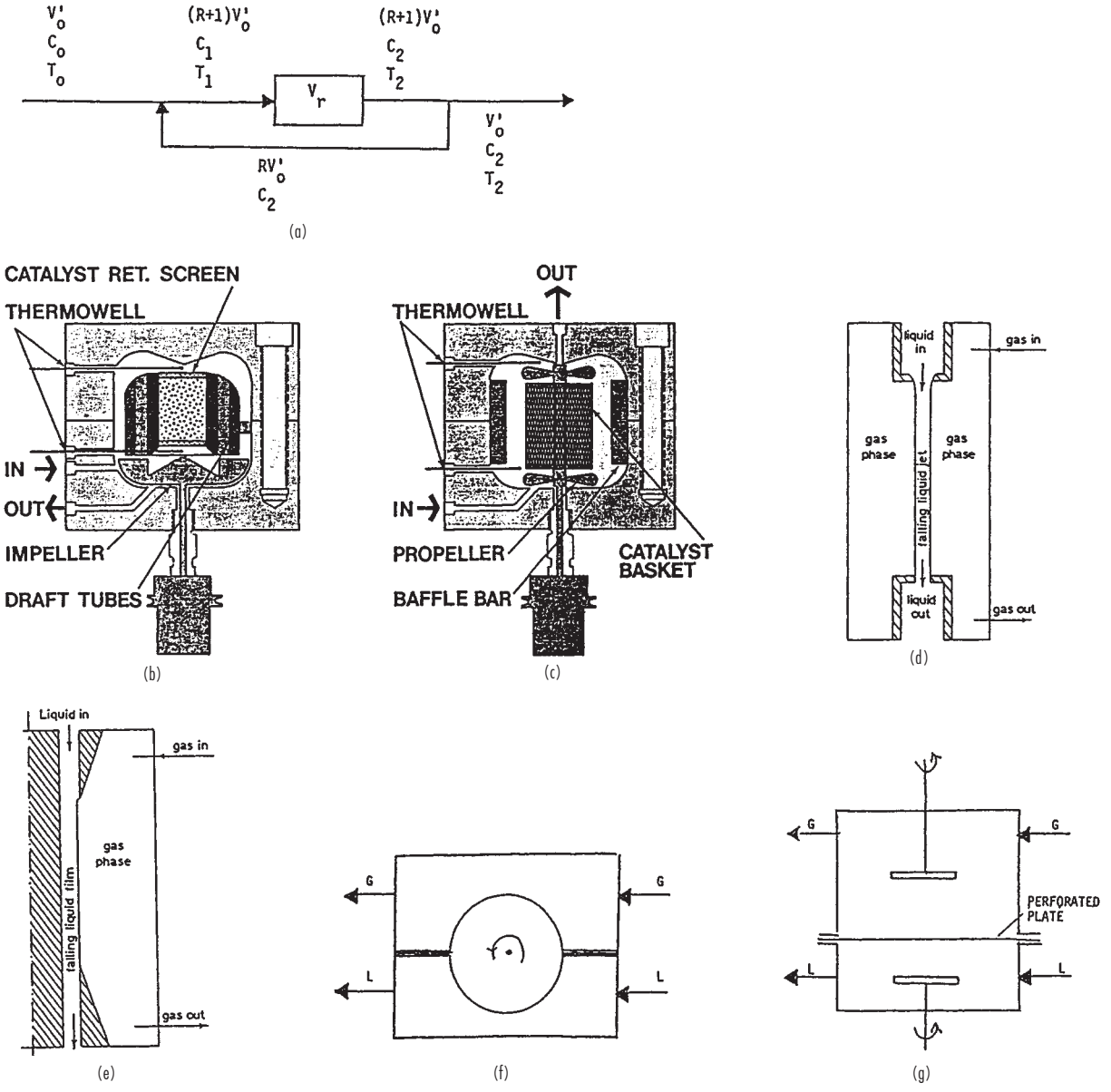


FIG. 23-29 Laboratory reactors for gas/liquid and fluid/solid processes. (*a*) Plug flow with external recycle, isothermal approach, $T_1 - T_2 = (T_0 - T_2)/(R + 1) \Rightarrow 0$. (*b*) Internal recycle, fixed basket. (*Berty, Autoclave Engineers Inc.*) (*c*) Rotating basket. (*Carberry, Autoclave Engineers Inc.*) (*d*) Falling liquid jet, known interfacial area, $t = 0.001–0.1$ s. (*e*) Falling film, $t = 0.1–0.25$ s. (*f*) Rotating drum, $t = 0.01–0.25$ s. (*Danckwerts,* Gas-Liquid Reactions, *McGraw-Hill, 1970.*) (*g*) L and G stirred, gradientless, $t = 1–10$ s. (*Levenspiel and Godfrey,* Chem. Eng. Sci., **29,** *1723 [1974].*)

Bubble sizes tend to a minimum regardless of power input because coalescence eventually sets in. Pure liquids are coalescing type; solutions with electrolytes are noncoalescing but their bubbles also tend to a minimum. Agitated bubble size in air/water is about 0.5 mm (0.020 in), holdup fractions are about 0.10 coalescing and 0.25 noncoalescing, but more elaborate correlations have been made.

Mass-transfer coefficients seem to vary as the 0.7 exponent on the power input per unit volume, with the dimensions of the vessel and impeller and the superficial gas velocity as additional factors. A survey of such correlations is made by van't Riet (*Ind. Eng. Chem. Proc. Des. Dev.,* **18,** 357 [1979]). Table 23-12 shows some of the results.

A basic stirred tank design is shown in Fig. 23-30. Height to diameter ratio is $H/D = 2$ to 3. Heat transfer may be provided through a jacket or internal coils. Baffles prevent movement of the mass as a whole. A draft tube enhances vertical circulation. The vapor space is about 20 percent of the total volume. A hollow shaft and impeller increase gas circulation (as in Fig. 23-31). A splasher can be attached to the shaft at the liquid surface to improve entrainment of gas. A variety of impellers is in use. The pitched propeller moves the liquid axially, the flat blade moves it radially, and inclined blades move it both axially and radially. The anchor and some other designs are suited to viscous liquids.

TABLE 23-11 Hydrocarbon Gas Treatments with Aqueous DEA*

Item	A	B	C	D	E
Absorber					
P, atm	68	14	7	15	12
T, °C			19	60	52
Trays	30	23	16		
Packing				26 ft, 3 in	30 ft, ¾
Stripper					
P, atm	2	2			
T, °C	133	118			
Trays	20	20			
Input					
CO_2	10%	0.35%			
H_2S gr/100 scf	15%	170	3,196	1,490	2,500
COS	300 ppm				
CS_2	600 ppm				
Output					
CO_2 gr/100 scf	1.6				
H_2S gr/100 scf	0.28	0.3	15	26	15
COS gr/100 scf	0				

*1 gr/100 scf = 0.0229 g/std m^3

TABLE 23-12 Correlations of Mass-Transfer Coefficients in Stirred Tanks

Correlations of Koetsier, et al. (*Chem. Eng. Journal,* **5,** 61, 71 [1973])

For coalescing liquids:

$$k_L a = 0.05\left(\frac{N^2 D_i^2}{D_t^{1.5}}\right)^{1.95} = 0.05\, E^{0.65}\left(\frac{D_i}{D_t}\right)^{0.65} D_t^{-0.33}, \qquad 1/s$$

$$k_L = 0.002\left(\frac{N D_i^2}{D_t^{1.6}} - 0.45\right), \qquad m/s$$

For noncoalescing liquids (electrolytes):

$$k_L a = 0.11\, E^{0.7}\left(\frac{D_i}{D_t}\right)^{0.7} D_t^{-0.35}$$

$$k_L = 0.000325\, E^{0.3}\left(\frac{D_i}{D_t}\right)^{0.7} D_t^{-0.35}$$

where N = revolutions/s
D_i = impeller diameter, m, 6-blade turbine
D_t = tank diameter, m
E = power input, kW/m^3

Correlation cited by Middleton (in Harnby, et al., *Mixing in the Process Industries,* Butterworth, 1985)

Coalescing:

$$k_L a = 1.2\, E^{0.7} u_s^{0.6}, \qquad 1/s$$

Noncoalescing:

$$k_L a = 2.3\, E^{0.7} u_s^{0.6}, \qquad 1/s$$

where u_s = superficial gas velocity, m/sec

For gas dispersion the six-bladed turbine is preferred. When the ratio of liquid height to diameter is $H/D \le 1$ a single impeller suffices, and in the range $1 \le H/D \le 1.8$ two are needed. The oil hydrogenator of Fig. 23-32, which is to scale, uses three impellers. The greater depth there will give longer contact time, which is desirable for slow reactions. The best position for inlet of gas is below and at the center of the impeller, or at the bottom of the draft tube. An open pipe is in common use, but a sparger may be helpful. A two-speed motor is desirable to prevent overloading, the lower speed to cut in when the gas supply is cut off but agitation is to continue, since gassed power requirement is significantly less than ungassed.

In tanks of 5.7 to 18.9 m^3 (1,500 to 5,000 gal) rotation speeds are from 50 to 200 rpm and power requirements are 2 to 75 hp; both depend on superficial velocities of gas and liquid (Hicks and Gates, *Chem. Eng.,* 141–148 [July 1976]). As a rough guide, power requirements and impeller tip speeds are as follows.

Operation	hp/1,000 gal*	Tip speed, ft/s
Homogeneous reaction	0.5–1.5	7.5–10
With heat transfer	1.5–5	10–15
Liquid/liquid mixing	5	15–20
Gas/liquid mixing	5–10	15–20

*1 hp/1,000 gal = 0.197 kw/m^3.

Hydrogenation of Oils in Stirred Tanks Large-scale uses of stirred tanks include the gas/liquid reactions of hydrogenation and fermentation. For hydrogenation of vegetable and animal oils, semibatch operations often are preferred to continuous ones because of the variety of feedstocks or product specifications or long reaction times or small production rates. Sketches of batch and continuous hydrogenators are shown in Figs. 23-32 and 23-33.

The composition of an oil and the progress of its hydrogenation is expressed in terms of its iodine value (IV). Edible oils are mixtures of unsaturated compounds with molecular weights in the vicinity of 300. The IV is a measure of this unsaturation. It is found by a standardized procedure. A solution of ICl in a mixture of acetic acid and carbon tetrachloride is mixed in with the oil and allowed to react to completion, usually for less than 1 h. Halogen addition takes place at the double bond, after which the amount of unreacted iodine is determined by analysis. The reaction is

$$ICl + RCH{=}CHR_1 \Rightarrow RCHI{-}CHClR_1$$

and the definition is

$$IV = \frac{I\ absorbed}{100\ g\ oil}$$

To start a hydrogenation process, the oil and catalyst are charged first, then the vessel is evacuated for safety and hydrogen is supplied continuously from storage and kept at some fixed pressure, usually in the range of 1 to 10 atm (14.7 to 147 psi). Internal circulation of

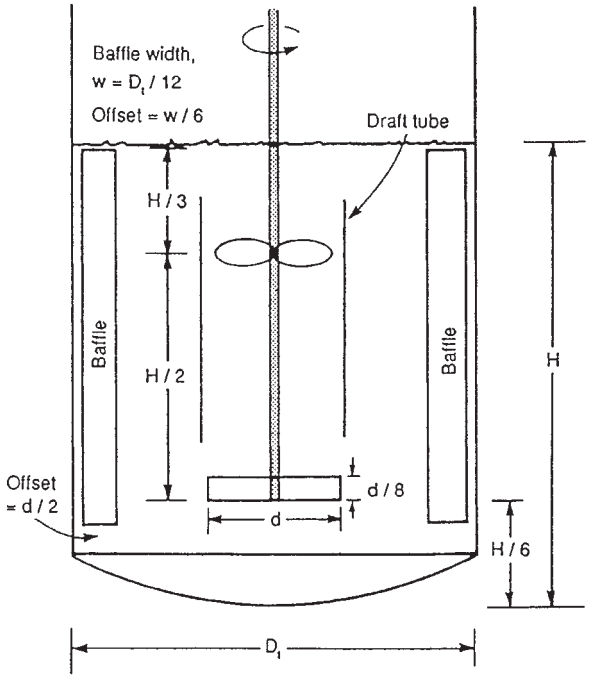


FIG. 23-30a A basic stirred tank design, not to scale, showing a lower radial impeller and an upper axial impeller housed in a draft tube. Four equally spaced baffles are standard. H = height of liquid level, D_t = tank diameter, d = impeller diameter. For radial impellers, $0.3 \le d/D_t \le 0.6$.

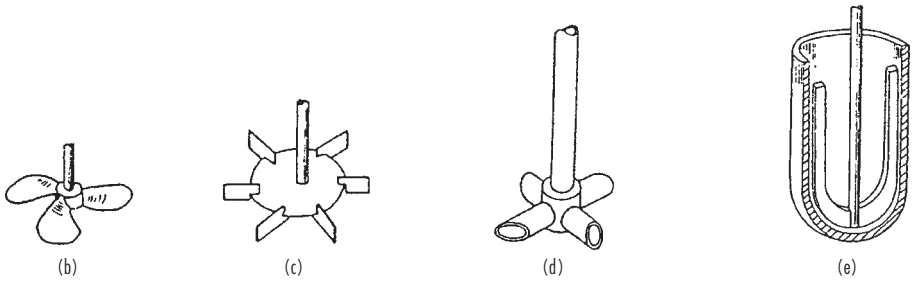


FIG. 23-30 Basic stirred tank design and selected kinds of impellers. (*b*) Propeller. (*c*) Turbine. (*d*) Hollow. (*e*) Anchor.

hydrogen is provided by axial and radial impellers or with a hollow impeller that throws the gas out centrifugally and sucks gas in from the vapor space through the hollow shaft. Some plants have external gas circulators. Reaction times are 1 to 4 h.

For edible oils the temperature is kept at about 180°C (356°F). Consumption of hydrogen per unit change of IV is

$$\frac{0.0795 \text{ kg } H_2}{1{,}000 \text{ kg oil}}$$

$$\frac{883.3 \text{ L STP } H_2}{1{,}000 \text{ kg oil}}$$

Solubility of hydrogen depends on the temperature and pressure but only slightly on the natures of the oils that are usually processed.

$$S = (0.04704 + 0.000294T)P, \quad \frac{\text{L STP}}{\text{kg oil}} \qquad (23\text{-}106)$$

with T in °C and P in atm.

Heat evolution is 0.94 to 1.10 kcal/(kg oil)(unit drop of IV) (1.69 to 1.98 Btu/[lbm oil][unit drop of IV]). Because space for heat-transfer coils in the vessel is limited, the process is organized to give a maximum IV drop of about 2.0/min. The rate of reaction, of course, drops off rapidly as the reaction proceeds, so a process may take several hours. The end point of a hydrogenation is a specified IV of the product, but the progress of a reaction before the end can be followed by measuring hardness or refractive index.

Saturation of the oil with hydrogen is maintained by agitation. The rate of reaction depends on agitation and catalyst concentration. Beyond a certain agitation rate, resistance to mass transfer is eliminated and the rate becomes independent of pressure. The effect of catalyst concentration also reaches limiting values. The effects of pressure and temperature on the rate are indicated by Fig. 23-34 and of catalyst concentration by Fig. 23-35. Reaction time is related to temperature, catalyst concentration, and IV in Table 23-13.

Nickel is the most used catalyst, 20 to 25 percent Ni on a porous siliceous support in the form of flakes that are readily filterable. The pores allow access of the reactants to the extended pore surface, which is in the range of 200 to 600 m^2/g (977×10^3 to $2{,}931 \times 10^3$ ft^2/lbm) of

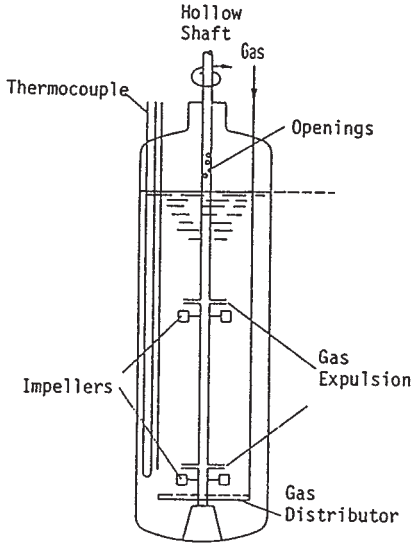


FIG. 23-31 Stirred tank with hollow shaft for hydrogenation of nitrocaprolactam. (*Dierendonk et al.,* 5th European Symp. Chem. React. Eng., *Pergamon, 1972, pp. B6–45.*)

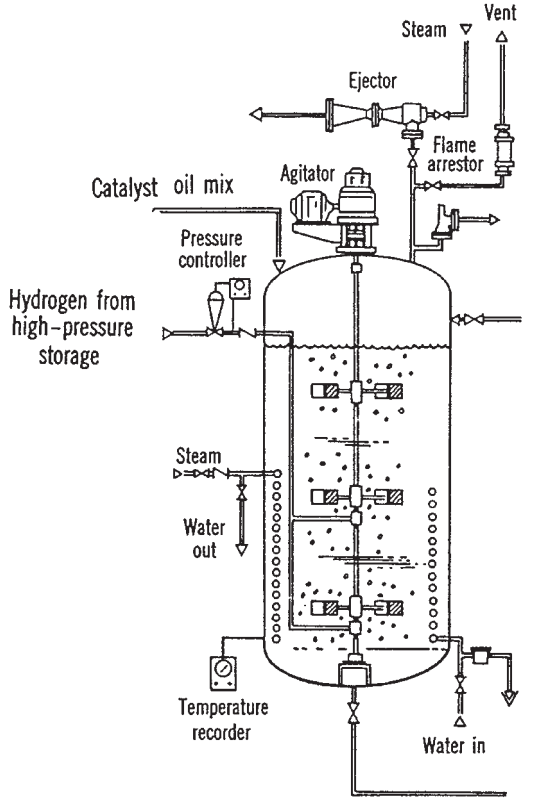


FIG. 23-32 Stirred tank hydrogenator for edible oils. (*Votator Division, Chemetron Corporation.*)

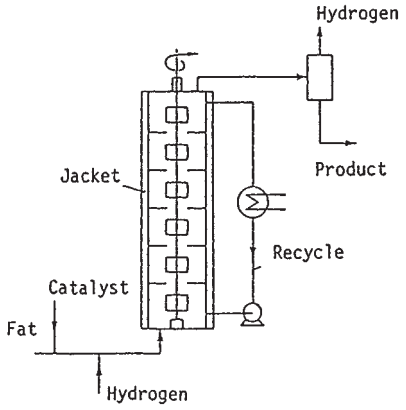


FIG. 23-33 Continuous hydrogenation of fats (*Albright,* Chem. Eng., ***74,*** *249* [*9 Oct. 1967*].)

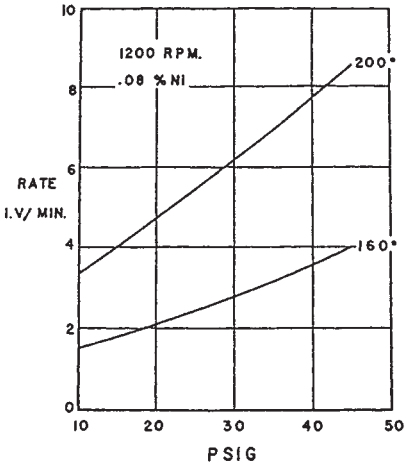


FIG. 23-34 Effect of reaction pressure and temperature on the rate of hydrogenation of soybean oil. (*Swern, ed.,* Bailey's Industrial Oil and Fat Products, *vol. 2, Wiley, 1979.*)

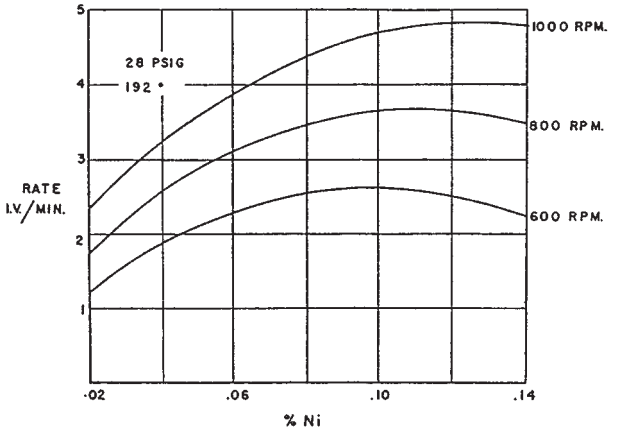


FIG. 23-35 Effect of catalyst concentration and stirring rate on hydrogenation of soybean oil. (*Swern, ed.,* Bailey's Industrial Fat and Oil Products, *vol. 2, Wiley, 1979.*)

TABLE 23-13 Time, Temperature, and Iodine Value of Tallow Hydrogenation*

	0.03% Ni, $P = 20$ atm		0.04% Ni, $P = 25$ atm		0.08% Ni, $P = 3$ atm	
t, min	*T*, °C	IV	*T*, °C	IV	*T*, °C	IV
0	140	42.3	140	44.1	160	42.3
5	145	39.7			165	35.0
10	150	37.3	147	38.0	170	27.8
30	160	27.1	160	26.6	180	8.4
60	180	14.5	180	13.4	200	1.7
90	190	5.4	180	5.6	200	0.3
120	200	1.0	180	0.5	200	0.25
180	200	0.3			200	0.1

*To convert atm to kPa, multiply by 101.3.

SOURCE: From Patterson, *Hydrogenation of Fats and Oils,* Applied Science Publishers, 1983.

which 20 to 30 percent is catalytically active. The concentration of catalyst in the slurry can vary over a wide range but is usually under 0.1% Ni. Catalysts are subject to degradation and poisoning, particularly by sulfur compounds. Accordingly, about 10 to 20 percent of the recovered catalyst is replaced by fresh before recycling. Other catalysts are applied in special cases. Expensive palladium has about 100 times the activity of nickel and is effective at lower temperatures.

While the liquid is saturated with hydrogen the reaction is pseudo-first-order. One sequence of reactions of acids that has been investigated (Swern, ed., *Bailey's Industrial Oil and Fat Products,* vol. 2, Wiley, 1979, p. 12) is

$$\text{Linolenic} \overset{1}{\Rightarrow} \text{Linoleic} \overset{2}{\Rightarrow} \text{Oleic} \overset{3}{\Rightarrow} \text{Stearic}$$

At 175°C (347°F), 0.02% Ni, 1 atm, 600 rpm the specific rates are: $k_1 = 0.367$, $k_2 = 0.159$, $k_3 = 0.013$/min.

Figure 23-36 shows a computer calculation with these specific rates, but which does not agree quantitatively with the figure shown by Swern. The time scales appear to be different, but both predict a peak in the amount of oleic acid and rapid disappearance of the first two acids.

A case study of the hydrogenation of cottonseed oil is made by Rase (*Chemical Reactor Design for Process Plants,* vol. 2, Wiley, 1977, pp. 161–178).

Semibatch hydrogenation of edible oils has a long history and a well-established body of practice by manufacturers and catalyst suppliers. Problems of new oils, new specifications, new catalyst poisons,

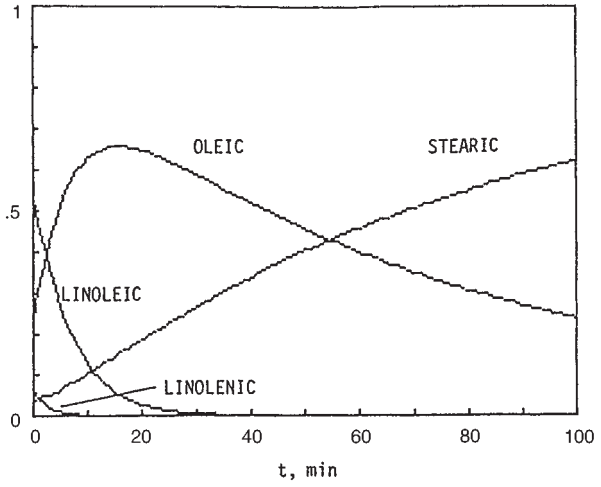


FIG. 23-36 Product compositions of the first-order sequence of fatty acids: Linolenic ⇒ Linoleic ⇒ Oleic ⇒ Stearic.

and even new scales of operation can probably be handled with a minimum amount of laboratory or pilot plant work.

Aerobic Fermentation The classic example of large-scale aerobic fermentation is the production of penicillin by the growth of a specific mold. Commercial vessel sizes are 40,000 to 200,000 L (1,400 to 7,000 ft^3). The operation is semibatch in that the lactose or glucose nutrient and air are charged at controlled rates to a precharged batch of liquid nutrients and cell mass. Reaction time is 5 to 6 days.

The broth is limited to 7 to 8 percent sugars, which is all the mold will tolerate. Solubility of oxygen is so limited that air must be supplied over a long period as it is used up. The pH is controlled at about 6.5 and the temperature at 24°C (75°F). The air is essential to the growth. Dissolved oxygen must be kept at a high level for the organism to survive. Air also serves to agitate the mixture and to sweep out the CO_2 and any noxious byproducts that are formed. Air supply is in the range of 0.5 to 1.5 volumes/(volume of liquid)(min). For organisms grown on glucose the oxygen requirement is 0.4 g/g dry weight; on methanol it is 1.2 g/g.

The heat of reaction requires cooling water at the rate of 10 to 40 L/(1,000 L holdup)(h). Vessels under about 500 L (17.6 ft^3) are provided with jackets, larger ones with coils. For a 55,000-L vessel, 50 to 70 m^2 may be taken as average.

Mechanical agitation is needed to break up the gas bubbles but must avoid rupturing the cells. The disk turbine with radial action is most suitable. It can tolerate a superficial gas velocity up to 120 m/h (394 ft/h) without flooding, whereas the propeller is limited to about 20 m/h (66 ft/h). When flooding occurs, the impeller is working in a gas phase and cannot assist the transfer of gas to the liquid phase. Power input by agitation and air sparger is 1 to 4 W/L (97 to 387 Btu/[ft^3·h]) of liquid.

Bubble Reactors In bubble columns the gas is dispersed by nozzles or spargers without mechanical agitation. In order to improve the operation, redispersion at intervals may be effected by static mixers, such as perforated plates. The liquid may be clear or be a slurry.

Because of their large volume fraction of liquid, bubble reactors are suited to slow reactions; that is, those whose rate of reaction is smaller than their rate of diffusion. Major advantages are the absence of moving parts, the ability to handle solid particles without erosion or plugging, good heat transfer at the wall or coils, high interfacial area, and high mass-transfer coefficients. A disadvantage is the occurrence of backmixing of the liquid phase and some of the gas phase, which may result in poor selectivity with some complex reactions. High pressure drop because of the static head of the liquid also is harmful. At high height/diameter ratios (>15), the effective interfacial area decreases rapidly. Generally, the tower height is greater than for tray or packed towers.

Two complementary reviews of this subject are by Shah et al. (*AIChE Journal,* **28,** 353–379 [1982]) and Deckwer (in de Lasa, ed., *Chemical Reactor Design and Technology,* Martinus Nijhoff, 1985, pp. 411–461). Useful comments are made by Doraiswamy and Sharma (*Heterogeneous Reactions,* Wiley, 1984). Charpentier (in Gianetto and Silveston, eds., *Multiphase Chemical Reactors,* Hemisphere, 1986, pp. 104–151) emphasizes parameters of trickle bed and stirred tank reactors. Recommendations based on the literature are made for several design parameters: namely, bubble diameter and velocity of rise, gas holdup, interfacial area, mass-transfer coefficients k_La and k_L but not k_g, axial liquid-phase dispersion coefficient, and heat-transfer coefficient to the wall. The effect of vessel diameter on these parameters is insignificant when $D \geq 0.15$ m (0.49 ft), except for the dispersion coefficient. Application of these correlations is to: (1) chlorination of toluene in the presence of $FeCl_3$ catalyst, (2) absorption of SO_2 in aqueous potassium carbonate with arsenite catalyst, and (3) reaction of butene with sulfuric acid to butanol.

Some qualitative observations can be made. Increase of the superficial gas velocity increases the holdup of gas, the interfacial area, and the overall mass-transfer coefficient. The ratio of height to diameter is not important in the range of 4 to 10. Increase of viscosity and decrease of surface tension increase the interfacial area. Electrolyte solutions have smaller bubbles, higher gas holdup, and higher interfacial area. Sparger design is unimportant for superficial gas velocities > 5 to 10 cm/s (0.16 to 0.32 ft/s). Gas conversion falls off at higher superficial velocities, so values under 10 cm/s (0.32 ft/s) are advisable.

The gas approximates plug flow except in wide columns, but the liquid undergoes considerable backmixing. The latter effect can be reduced with packing or perforated plates. The effect on selectivity may become important. In the oxidation of liquid *n*-butane, for instance, the ratio of methyl ethyl ketone to acetic acid is much higher in plug flow than in mixed. Similarly, in the air oxidation of isobutane to *tert*-butyl hydroperoxide, where *tert*-butanol also is obtained, plug flow is more desirable.

Bubble action provides agitation about equivalent to that of mechanical stirrers, and thus about the same heat-transfer coefficients.

In cases of high liquid velocities (>30 cm/s [0.98 ft/s]) and low gas velocities (1 to 3 cm/s [0.033 to 0.098 ft/s]) it is advantageous to have concurrent downward flow.

Pulsations can improve performance. According to Baird and Garstang (*Chem. Eng. Sci.,* **22,** 1663 [1967]; **27,** 823 [1972]) at low gas velocity (0.8 to 2.4 cm/s [0.026 to 0.079 ft/s]) the value of k_La can be increased by as much as three-fold by pulsations.

Packed bubble columns operate with flooded packing, in contrast with normal packed columns which usually operate below 70 percent of the flooding point. With packing, liquid backmixing is reduced and interfacial area is increased 15 to 80 percent, but the true mass-transfer coefficient remains the same. The installation of perforated plates or grids at intervals also reduces liquid backmixing. At relatively high superficial gas velocities (10 to 15 cm/s [0.33 to 0.49 ft/s]) mixing between zones is small so the vessel performs as a CSTR battery. Radial baffles (also called disk-and-doughnut baffles) are also helpful. One set of rules is that the hole should be about 0.7 times the vessel diameter and the spacing should be 0.8 times the diameter.

Liquid Dispersion Spray columns are used with slurries or when the reaction product is a solid. The absorption of SO_2 by a lime slurry is an example. In the treatment of phosphate rock with sulfuric acid, offgases contain HF and SiF_4. In a spray column with water, solid particles of fluorosilic acid are formed but do not harm the spray operation. The coefficient k_L in spray columns is about the same as in packed columns, but the spray interfacial area is much lower. Considerable backmixing of the gas also takes place, which helps to make the spray volumetrically inefficient. Deentrainment at the outlet usually is needed.

In Venturi scrubbers the gas is the motive fluid. This equipment is of simple design and is able to handle slurries and large volumes of gas, but the gas pressure drop may be high. When the reaction is slow, further holdup in a spray chamber is necessary.

In liquid ejectors or aspirators, the liquid is the motive fluid, so the gas pressure drop is low. Flow of slurries in the nozzle may be erosive. Otherwise, the design is as simple as that of the Venturi.

The application of liquid dispersion reactors to the absorption of fluorine gases is described by Kohl and Riesenfeld (*Gas Purification,* Gulf, 1985, pp. 268–288).

Tubular Reactors In a tubular reactor with concurrent flow of gas and liquid, the variety of flow patterns ranges from a small quantity of bubbles in the liquid to small quantities of droplets in the gas, depending on the rates of the two streams. Figure 23-25 shows the patterns in horizontal flow; those in vertical flow are a little different. This equipment has good heat transfer, accommodates wide ranges of *T* and *P,* and is primarily in plug flow, and the high velocities prevent settling of slurries or accumulations on the walls. Mixing of the phases can be improved by helical static mixing inserts like those made by Kenics Corporation and others.

The reasons why a tubular reactor was selected for the production of adipic acid nitrile from adipic acid and ammonia are discussed by Weikard (in Ullmann, *Enzyklopaedie,* 4th ed., vol. 3, Verlag Chemie, 1973, p. 381).

1. The process has a large Hatta number; that is, the rate of reaction is much greater than the rate of diffusion, so a large interfacial area is desirable for carrying out the reaction in the film.
2. With normal excess ammonia the gas/liquid ratio is about 3,500 m^3/m^3. At this high ratio there is danger of fouling the surface with tarry reaction products. The ratio is brought down to a more satisfactory value of 1,000 to 1,500 by recycle of some of the effluent.
3. High selectivity of the nitrile is favored by short contact time.
4. The reaction is highly endothermic so heat input must be at a high rate.

Points 2 and 4 are the main ones governing the choice of reactor type. The high gas/liquid ratio restricts the choice to types *d, e, i,* and *k* of Fig. 23-25, but because of the high rate of heat transfer that is needed the choice falls to the falling film or tubular types.

The final selection was a tubular reactor with upward concurrent flow, with liquid holdup of 20 to 30 percent, and with residence times of 1.0 s for gas and 3 to 5 min for liquid.

Reaction in a Centrifugal Pump In the reaction between acetic acid and gaseous ketene to make acetic anhydride, the pressure must be kept low (0.2 atm) to prevent polymerization of ketene. A packed tower with low pressure drop could be used but the required volume is very large because of the low pressure. Spes (*Chem. Ing. Tech.,* **38,** 963–966 [1966]) selected a centrifugal pump reactor where compression to atmospheric pressure does take place but the contact time is too short for polymerization yet long enough for the reaction to occur. The reaction product is cooled in an external unit and partly recycled for temperature control.

Falling Film Reactor Dodecylbenzene sulfonic acid is made by reacting 5 to 10% SO_3 in air with dodecylbenzene. The gas/liquid ratio is about 1,000 m^3/m^3, and the product is highly viscous. Process requirements are a short contact time, a high rate of heat removal (170 kJ/g mol) and minimum backmixing of the liquid phase to avoid byproducts. To satisfy these requirements, a falling film reactor was selected by Ujidhy, Babos, and Farady (*Chemische Technik,* **18,** 652–654 [1966]). The gas velocity was made 12 to 15 m/s (39 to 49 ft/s) through a narrowed passage counter to the liquid flow.

LIQUID/LIQUID REACTIONS

Liquid/liquid reactions of industrial importance are fairly numerous. A list of 26 classes of reactions with 61 references has been compiled by Doraiswamy and Sharma (*Heterogeneous Reactions,* Wiley, 1984). They also indicate the kind of reactor normally used in each case. The reactions range from such prosaic examples as making soap with alkali, nitration of aromatics to make explosives, and alkylation of C_4s with sulfuric acid to make improved gasoline, to some much less familiar operations.

EQUIPMENT

Equipment suitable for reactions between liquids is represented in Fig. 23-37. Almost invariably, one of the phases is aqueous with reactants distributed between phases; for instance, NaOH in water at the start and an ester in the organic phase. Such reactions can be carried out in any kind of equipment that is suitable for physical extraction, including mixer-settlers and towers of various kinds: empty or packed, still or agitated, either phase dispersed, provided that adequate heat transfer can be incorporated. Mechanically agitated tanks are favored because the interfacial area can be made large, as much as 100 times that of spray towers, for instance. Power requirements for L/L mixing are normally about 5 hp/1,000 gal and tip speeds of turbine-type impellers are 4.6 to 6.1 m/s (15 to 20 ft/s).

Table 23-14 gives data for common types of L/L contactors. Since the given range of k_La is more than 100/1, this information is not of direct value for sizing of equipment. The efficiencies of various kinds of small liquid/liquid contactors are summarized in Fig. 23-38. Larger units may have efficiencies of less than half these values.

MECHANISMS

Few mechanisms of liquid/liquid reactions have been established, although some related work such as on droplet sizes and power input has been done. Small contents of surface-active and other impurities in reactants of commercial quality can distort a reactor's predicted performance. Diffusivities in liquids are comparatively low, a factor of 10^5 less than in gases, so it is probable in most industrial examples that they are diffusion controlled. One consequence is that L/L reactions may not be as temperature sensitive as ordinary chemical reactions, although the effect of temperature rise on viscosity and droplet size can result in substantial rate increases. L/L reactions will exhibit behavior of homogeneous reactions only when they are very slow, nonionic reactions being the most likely ones. On the whole, in the present state of the art, the design of L/L reactors must depend on scale-up from laboratory or pilot plant work.

Particular reactions can occur in either or both phases or near the interface. Nitration of aromatics with HNO_3-H_2SO_4 occurs in the aqueous phase (Albright and Hanson, eds., *Industrial and Laboratory Nitrations,* ACS Symposium Series **22** [1975]). An industrial example of reaction in both phases is the oxidation of cyclohexanone, a step in the manufacture of caprolactam for nylon (Rod, *Proc. 4th International/6th European Symposium on Chemical Reactions,* Heidelberg, Pergamon, 1976, p. 275). The reaction between butene and isobutane to form isooctane in the presence of sulfuric acid is judged to occur at the acid/hydrocarbon interface, although side reactions to form higher hydrocarbons may occur primarily in the acid phase (Albright, in Albright and Goldsby, eds., *Industrial and Laboratory Nitrations,* ACS Symposium Series **55,** 145 [1977]). The formation of dioxane from isobutene in a hydrocarbon phase and aqueous formaldehyde occurs preponderantly in the aqueous phase where the rate equation is first-order in formaldehyde, although the specific rate is also proportional to the concentration of isobutene in the organic phase (Hellin et al., *Genie. Chim.,* **91,** 101 [1964]).

Reactions involving ions can be favored to occur in the organic phase by use of phase-transfer catalysts. Thus the conversion of 1-chlorooctane to 1-cyanooctane with aqueous NaCN is vastly accelerated in the organic phase by 1.3 percent of tributyl (hexadecyl) phosphonium bromide in the aqueous phase. (Starks and Owens, *J. Am. Chem. Soc.,* **95,** 3613 [1973]). A large class of such promotions is known.

There are instances where an extractive solvent is employed to force completion of a reversible homogeneous reaction by removing the reaction product. In the production of KNO_3 from KCl and HNO_3, for instance, the HCl can be removed continuously from the aqueous phase by contact with amyl alcohol, thus forcing completion (Baniel and Blumberg, *Chim. Ind.,* **4,** 27 [1957]).

OPERATING DATA

Not many operating data of large-scale liquid/liquid reactions are published. One study was made of the hydrolysis of fats with water at 230 to 260°C (446 to 500°F) and 41 to 48 atm (600 to 705 psi) in a continuous commercial spray tower. A small amount of water dissolved in the fat and reacted to form an acid and glycerine. Then most of the glycerine migrated to the water phase. The tower was operated at about 18 percent of flooding, at which condition the HETS was found to be about 9 m (30 ft) compared with an expected 6 m (20 ft) for purely physical extraction (Jeffreys, Jenson, and Miles, *Trans. Inst. Chem. Eng.,* **39,** 389–396 [1961]). A similar mathematical treatment of a batch hydrolysis is made by Jenson and Jeffreys (*Inst. Chem. Engrs. Symp. Ser.,* No. 23 [1967]).

LABORATORY STUDIES

For many laboratory studies, a suitable reactor is a cell with independent agitation of each phase and an undisturbed interface of known area, like the item shown in Fig. 23-29*d.* Whether a rate process is controlled by a mass-transfer rate or a chemical reaction rate sometimes can be identified by simple parameters. When agitation is sufficient to produce a homogeneous dispersion and the rate varies with further increases of agitation, mass-transfer rates are likely to be significant. The effect of change in temperature is a major criterion: a rise of 10°C (18°F) normally raises the rate of a chemical reaction by a factor of 2 to 3, but the mass-transfer rate by much less. There may be instances, however, where the combined effect on chemical equilibrium, diffusivity, viscosity, and surface tension also may give a comparable enhancement.

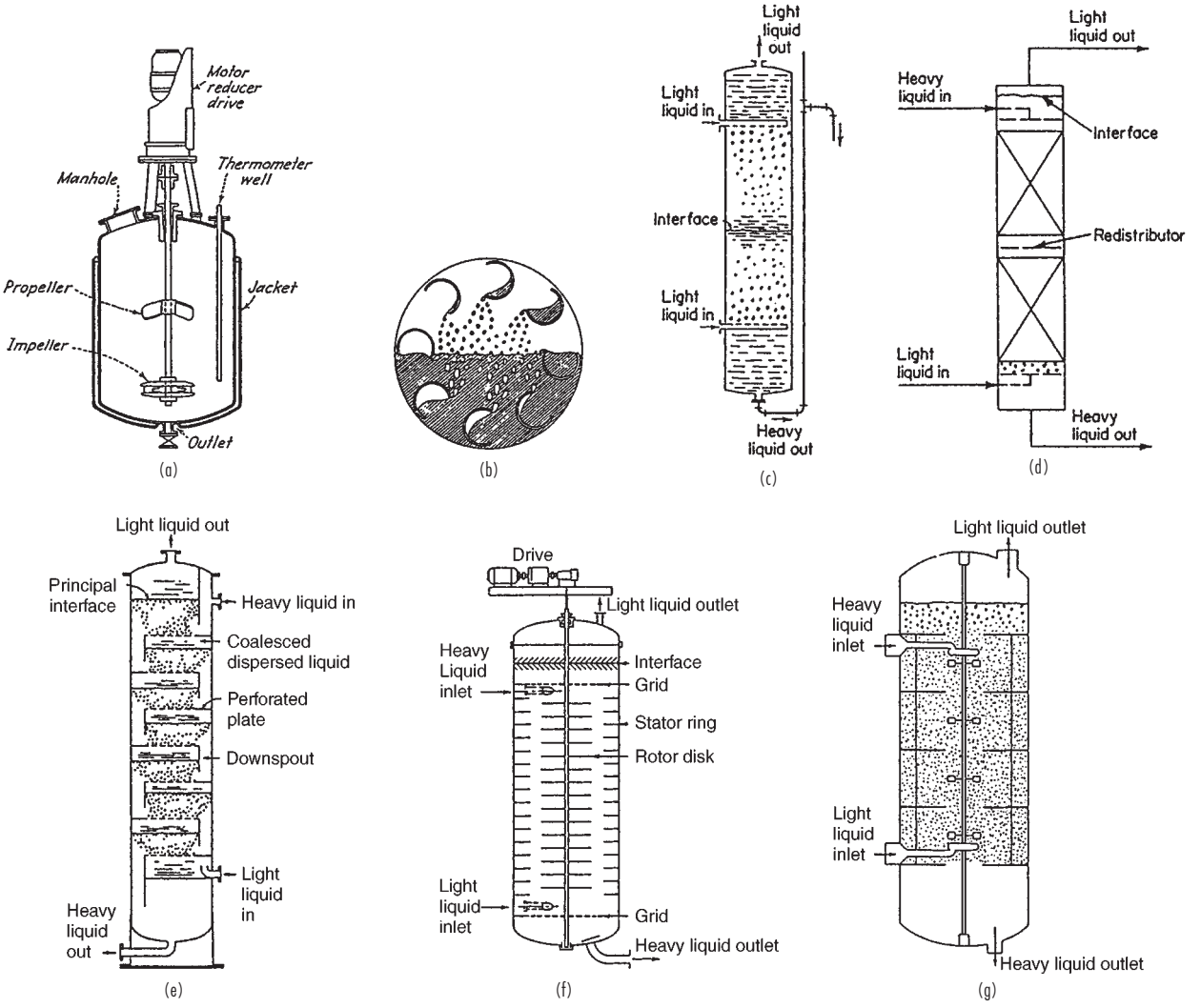


FIG. 23-37 Equipment for liquid/liquid reactions. (*a*) Batch stirred sulfonator. (*b*) Raining bucket (*RTL S A, London*). (*c*) Spray tower with both phases dispersed. (*d*) Two-section packed tower with light phase dispersed. (*e*) Sieve tray tower with light phase dispersed. (*f*) Rotating disk contactor (RDC) (*Escher B V, Holland*). (*g*) Oldshue-Rushton extractor (*Mixing Equipment Co.*).

For a chemically controlled process, conversion depends only on the residence time and not on which phase is dispersed, whereas the interfacial area and, consequently, the rate of mass transfer will change when the relative volumes of the phases are changed. If a reaction is known to occur in a particular phase, and the conversion is found to depend on the residence time in that phase, chemical reaction is controlling.

Laboratory investigations may possibly establish reaction mechanisms, but quantitative data for design purposes require pilot plant work with equipment of the type expected to be used in the plant.

TABLE 23-14 Continuous-Phase Mass-Transfer Coefficients and Interfacial Areas in Liquid/Liquid Contactors*

Type of equipment	Dispersed phase	Continuous phase	ε_D	τ_D	$k_L \times 10^2$, cm/s	a, cm^2/cm^3	$k_L a \times 10^2$, s^{-1}
Spray columns	P	M	0.05–0.1	Limited	0.1–1	1–10	0.1–10
Packed columns	P	P	0.05–0.1	Limited	0.3–1	1–10	0.3–10
Mechanically agitated contactors	PM	M	0.05–0.4	Can be varied over a wide range	0.3–1	1–800	0.3–800
Air-agitated liquid/liquid contactors	PM	M	0.05–0.3	Can be varied over a wide range	0.1–0.3	10–100	1.0–30
Two-phase cocurrent (horizontal) contactors	P	P	0.05–0.2	Limited	0.1–1.0	1–25	0.1–25

*P = plug flow, M = mixed flow, ε_D = fractional dispersed phase holdup, τ_D = residence time of the dispersed phase.
SOURCE: From Doraiswamy and Sharma, *Heterogeneous Reactions*, Wiley, 1984.

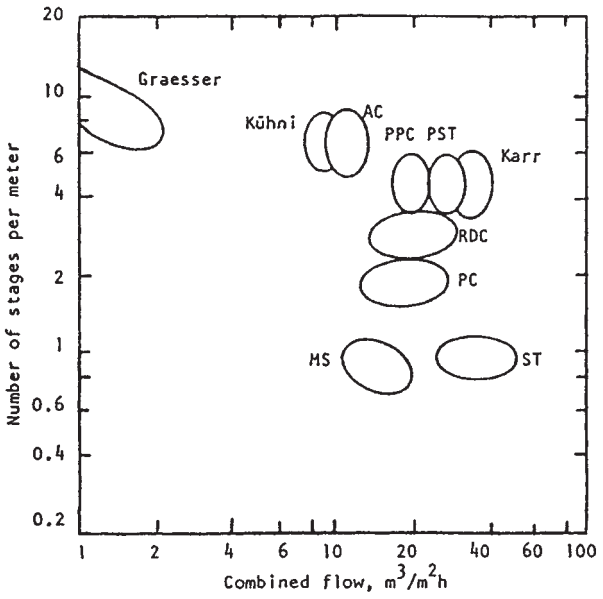


FIG. 23-38 Efficiency and capacity range of small-diameter extractors, 50 to 150 mm diameter. Acetone extracted from water with toluene as the disperse phase, $V_d/V_c = 1.5$. Code: AC = agitated cell; PPC = pulsed packed column; PST = pulsed sieve tray; RDC = rotating disk contactor; PC = packed column; MS = mixer-settler; ST = sieve tray. (*Stichlmair,* Chem. Ing. Tech. ***52***(*3*), *253–255* [*1980*]).

MASS-TRANSFER COEFFICIENTS

When liquid/liquid contactors are used as reactors, values of their mass-transfer coefficients may be enhanced by reaction, analogously to those of gas/liquid processes, but there do not seem to be any published data of this nature.

Mass-transfer coefficients and other characteristics of some types of liquid/liquid contactors are summarized in Table 23-14, which may be compared with Tables 23-9 and 23-10 for gas-liquid contactors. Efficiencies of several kinds of small-scale extractors are shown in Fig. 23-38. Larger-diameter equipment may have less than one-half these efficiencies. Spray columns are inefficient and are used only when other kinds of equipment could become clogged. Packed columns as liquid/liquid reactors are operated at 20 percent of flooding. Their HETS range from 0.6 to 1.2 m (1.99 to 3.94 ft). Sieve trays minimize backmixing and provide repeated coalescence and redispersion. Mixer-settlers provide approximately one theoretical stage, but several stages can be incorporated in a single shell, although with some loss of operating flexibility. The HETS of rotating disk contactor (RDC) is 1 to 2 m (3.2 to 6.4 ft). More elaborate staged extractors bring this down to 0.35 to 1.0 m (1.1 to 3.3 ft).

CHOICE OF DISPERSED PHASE

It is difficult to disperse a liquid when it occupies more than 75 percent of the volume. Otherwise, either liquid can be made continuous in a stirred tank by charging that liquid first, starting the agitator, and introducing the liquid to be dispersed. Customarily, the phase with the higher volumetric rate is dispersed since a larger interfacial area results in this way with a given droplet size. When a reactant diffuses away from a phase, that phase should be dispersed since the travel path then will be lower. In equipment that is subject to backmixing, such as spray or packed towers but not tray towers, the dispersed phase is the one with the smaller volumetric rate. When a substantial difference is known to exist for the two phases, the high phase resistance should be compensated for with increased surface by dispersion. The continuous phase should be the one that wets the material of construction. Usually, it is best to disperse a highly viscous phase. Since the holdup of continuous phase is greater, the phase that is less hazardous or less expensive should be continuous.

Experimentally, both modes probably should be tried. In the alkylation of C_4s with sulfuric acid, for instance, the continuous emulsion of acid produces a much better product and consumes less acid.

REFERENCES FOR LIQUID/LIQUID REACTORS

Hanson, C., ed., *Recent Advances in Liquid-Liquid Extraction,* Pergamon, 1971, pp. 429–453. Lo, T. C., M. H. I. Baird, and C. Hanson, eds., *Handbook of Solvent Extraction,* Wiley, 1983, pp. 37–52, 615–618. Rase, H. F., *Chemical Reactor Design for Process Plants,* vol. 1, Wiley, 1977, pp. 715–733.

GAS/LIQUID/SOLID REACTIONS

In many important cases of reactions involving gas, liquid, and solid phases, the solid phase is a porous catalyst. It may be in a fixed bed or it may be suspended in the fluid mixture. In general, the reaction occurs either in the liquid phase or at the liquid/solid interface. In fixed-bed reactors the particles have diameters of about 3 mm (0.12 in) and occupy about 50 percent of the vessel volume. Diameters of suspended particles are limited to 0.1 to 0.2 mm (0.004 to 0.008 in) minimum by requirements of filterability and occupy 1 to 10 percent of the volume in stirred vessels.

A list of 74 GLS reactions with literature references has been compiled by Shah (*Gas-Liquid-Solid Reactions,* McGraw-Hill, 1979), classified into groups where the solid is a reactant, or a catalyst, or inert. A list of 75 reactions made by Ramachandran and Chaudhari (*Three-Phase Chemical Reactors,* Gordon and Breach, 1983) identifies reactor types, catalysts, temperature, and pressure. They classify the processes according to hydrogenation of fatty oils, hydrodesulfurization, Fischer-Tropsch reactions, and miscellaneous hydrogenations and oxidations.

Some contrasting characteristics of the main kinds of three-phase reactors are summarized in Table 23-15. In *trickle bed reactors* both phases usually flow down, the liquid as a film over the packing. In *flooded reactors,* the gas and liquid flow upward through a fixed bed. *Slurry reactors* keep the solids in suspension mechanically; the overflow may be a clear liquid or a slurry, and the gas disengages from the vessel. The fluidized three-phase mixture is pumped through an *entrained solids reactor* and the effluent is separated into its phases in downstream equipment. In petroleum cracking technology this kind of equipment is called a *transfer line reactor.* In *fluidized bed reactors,* a stable bed of solids is maintained in the vessel and only the fluid phases flow through, except for entrained very fine particles. Most of the concern in this section is with trickle bed reactors, but some superior features of the other types are cited.

OVERALL RATE EQUATIONS WITH DIFFUSIONAL RESISTANCES

Say the concentration of dissolved gas A is A°. The series rates involved are from the gas to the interface where the concentration is A_i and from the interface to the surface of catalyst where the concentration is A_s and where the reaction rate is $\eta w k_m A_s^m$. At steady state,

$$r_A = k_L a_B (A^\circ - A_i) = k_s a_p (A_i - A_s) = \eta w k_m A_s^m \qquad (23\text{-}107)$$

For a first-order reaction, $m = 1$, the catalyst effectiveness η is independent of A_s, so that after elimination of A_i and A_s the explicit solution for the rate is

$$r_A = A^\circ \left[\frac{1}{k_L a_B} + \frac{1}{k_s a_p} + \frac{1}{\eta w k_1} \right]^{-1} \qquad (23\text{-}108)$$

TABLE 23-15 Characteristics of Gas/Liquid/Solid Reactors

Property	Trickle bed	Flooded	Stirred tank	Entrained solids	Fluidized bed
Gas holdup	0.25–0.45	Small	0.2–0.3		
Liquid holdup	0.05–0.25	High	0.7–0.8		
Solid holdup	0.5–0.7		0.01–0.10		0.5–0.7
Liquid distribution	Good only at high liquid rate		Good	Good	Good
RTD, liquid phase	Narrow	Narrower than for entrained solids reactor	Wide	Wide	Narrow
RTD, gas phase	Nearly plug flow		Backmixed	Backmixed	Narrow
Interfacial area	20–50% of geometrical	Like trickle bed reactor	100–1,500 m^2/m^3	100–400 m^2/m^3	Less than for entrained solids reactor
MTC, gas/liquid	High		Intermediate		
MTC, liquid/solid	High		High		
Radial heat transfer	Slow		Fast	Fast	Fast
Pressure drop	High with small d_p		Hydrostatic head		

Analytical solutions also are possible when η is constant and $m = 0$, ½, or 2. More complex chemical rate equations will require numerical solutions. Such rate equations are applied to the sizing of plug flow, CSTR, and dispersion reactor models by Ramachandran and Chaudhari (*Three-Phase Chemical Reactors,* Gordon and Breach, 1983).

TRICKLE BEDS

The catalyst is a fixed bed. Flows of gas and liquid are cocurrent downwards. Liquid feed is at such a low rate that it is distributed over the packing as a thin film and flows by gravity, helped along by the drag of the gas. This mode is suited to reactions that need only short reaction times, measured in seconds, short enough to forestall undesirable side reactions such as carbon formation. In the simplest arrangement the liquid distributor is a perforated plate with about 10 openings/dm^2 (10 openings/15.5 in^2) and the gas enters through several risers about 15 cm (5.9 in) high. More elaborate distributor caps also are used. Thicknesses of liquid films have been estimated to vary between 0.01 and 0.2 mm (0.004–0.008 in).

Liquid holdup is made up of a dynamic fraction, 0.03 to 0.25, and a stagnant fraction, 0.01 to 0.05. The high end of the stagnant fraction includes the liquid that partially fills the pores of the catalyst. The effective gas/liquid interface is 20 to 50 percent of the geometric surface of the particles, but it can approach 100 percent at high liquid loads with a consequent increase of reaction rate as the amount of wetted surface changes.

Both phases are substantially in plug flow. Dispersion measurements of the liquid phase usually report Peclet numbers, $u_l d_p/D$, less than 0.2. With the usual small particles, the wall effect is negligible in commercial vessels of a meter or so in diameter, but may be appreciable in lab units of 50 mm (1.97 in) diameter. Laboratory and commercial units usually are operated at the same space velocity, LHSV, but for practical reasons the lengths of lab units may be only 0.1 those of commercial units.

Countercurrent gas flow is preferred in pollution control when removal of gaseous impurities is desired.

Trickle Bed Hydrodesulfurization The first large-scale application of trickle bed reactors was to the hydrodesulfurization of petroleum oils in 1955. The temperature is elevated to enhance the specific rate and the pressure is elevated to improve the solubility of the hydrogen. A large commercial reactor may have 20 to 25 m (66 to 82 ft) total depth of catalyst, and may be up to 3 m (9.8 ft) diameter in several beds of 3 to 6 m (9.8 to 19.7 ft), limited by the crushing strength of the catalyst and the need for cold shots. Each bed is adiabatic, but the rise in temperature usually is limited to 30°C (86°F) by injection of cold hydrogen between beds. Conditions depend on the boiling range of the oil. Pressures are 34 to 102 atm (500 to 1,500 psi), temperatures 345 to 425°C (653 to 797°F). Catalyst granules are 1.5 to 3.0 mm (0.06 to 0.12 in), sometimes a little more. Catalysts are 10 to 20 percent Co and Mo on alumina.

Limiting flow rates are listed in Table 23-16. The residence times of the combined fluids are figured for 50 atm (735 psi), 400°C (752°F), and a fraction free volume between particles of 0.4. In a 20-m (66-ft) depth, accordingly, the contact times range from 6.9 to 960 s in commercial units. In pilot units the packing depth is reduced to make the contact times about the same.

An apparent first-order specific rate increases with liquid rate as the fraction of wetted surface improves. Catalyst effectiveness of particles 3 to 5 mm (0.12 to 0.20 in) diameter has been found to be about 40 to 60 percent.

A case study has been made (Rase, *Chemical Reactor Design for Process Plants,* vol. 2, Wiley, 1977, pp. 179–182) for removing 50 percent of the 1.9 percent sulfur from a 0.92 SG oil at the rate of 24,000 bbl/d with 2,300 SCF H_2/bbl at 375°C (707°F) and 50 atm (735 psi). For a particular catalyst, the bed height was 8.75 m (29 ft) and the diameter 2.77 m (9.09 ft).

Figure 23-39 is a sketch of a unit to handle 20,000 bbl/d of a light cracker oil with a gas stream containing 75% H_2. Liquid rate was 115,000 kg/h (253,000 lbm/h), gas rate 12,700 kg/hr (28,000 lbm/h), catalyst charge 40,000 kg (88,000 lbm) or 45 m^3 (1600 ft^3), LHSV ≅ 3. Operating conditions were 370°C (698°F) and 27 atm (397 psi). Vessel dimensions were not revealed, but with an $H/D = 5$, the catalyst bed will have the dimensions 2.25 × 11.25 m (7.38 × 36.9 ft).

FLOODED FIXED BED REACTORS

When the gas and liquid flows are cocurrent upward, a screen is needed at the top to retain the catalyst particles. Such a unit has been used for the hydrogenation of nitro and double bond compounds and

TABLE 23-16 Hydrodesulfurization Feed Rates of Gas and Liquid and Residence Times of the Mixture

	Superficial liquid velocity		Superficial gas velocity ft/h (STP)		Superficial gas velocity kg/m^2·s		Residence time s/m	
	ft/h	kg/m^2·s	A*	B*	A*	B*	A	B
Pilot plant†	1–30	0.08–2.5	180–5,400	890–27,000	0.0013–0.040	0.0066–0.20	480–16	97–3.5
Commercial reactor	10–300	0.8–25	1,800–54,000	8900–270,000	0.013–0.40	0.066–2.0	48–1.6	9.7–0.35

*The values of gas velocity are shown for (A) 1,000 and (B) 5,000 std ft^3 of H_2 per barrel, assuming that all the oil is in the liquid phase. To convert ft^3/bbl to m^3/m^3, multiply by 0.178.

†The length of the pilot-plant reactor was assumed to be one-tenth the length of the commercial reactor.

SOURCE: Partly after Satterfield, *AIChE Journal,* **21,** 209–228 (1975).

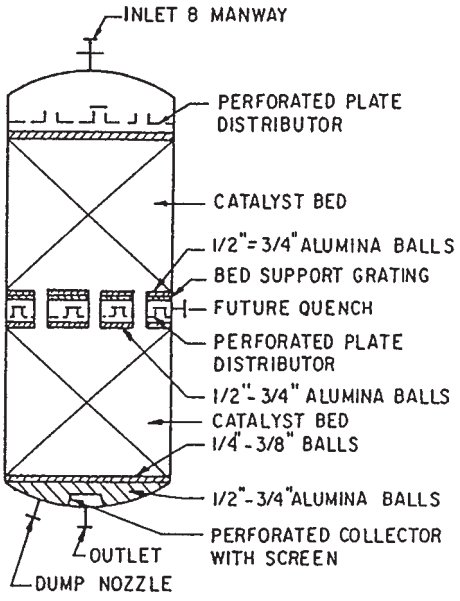


FIG. 23-39 Trickle bed reactor for hydrotreating 20,000 bbl/d of light catalytic cracker oil at 370°C and 27 atm. To convert atm to kPa, multiply by 101.3. (*Gianetto and Silveston,* Multiphase Chemical Reactors, *Hemisphere, 1986, pp. 533–563.*)

nitriles (Ovcinnikov et al., *Brit. Chem. Eng.,* **13,** 1,367 [1968]). High gas rates can cause movement and attrition of the particles. Accordingly, such equipment is restricted to low gas flow rates; for instance, where a hydrogen atmosphere is necessary but the consumption of hydrogen is slight. Backmixing is substantial in commercial-size columns, but less than in bubble columns. Liquid distribution is not a problem, and heat transfer is much better than in the trickle vessel. Liquid holdup and residence times are greater under flooding conditions, which may encourage side reactions.

Downward flow of both fluids imposes no restriction on the gas rate, except that the pressure drop will be high. On the whole, the trickle bed is preferred to the flooded bed.

SUSPENDED CATALYST BEDS

There are three main types of three-phase (GLS) reactors in which the catalyst particles move about in the fluid, as follows.

Slurry Reactors with Mechanical Agitation The catalyst may be retained in the vessel or it may flow out with the fluid and be separated from the fluid downstream. In comparison with trickle beds, high heat transfer is feasible, and the residence time can be made very great. Pressure drop is due to sparger friction and hydrostatic head. Filtering cost is a major item.

Entrained Solids Bubble Columns with the Solid Fluidized by Bubble Action The three-phase mixture flows through the vessel and is separated downstream. Used in preference to fluidized beds when catalyst particles are very fine or subject to disintegration in process.

GLS Fluidized with a Stable Level of Catalyst Only the fluid mixture leaves the vessel. Gas and liquid enter at the bottom. Liquid is continuous, gas is dispersed. Particles are larger than in bubble columns, 0.2 to 1.0 mm (0.008 to 0.04 in). Bed expansion is small. Bed temperatures are uniform within 2°C (3.6°F) in medium-size beds, and heat transfer to embedded surfaces is excellent. Catalyst may be bled off and replenished continuously, or reactivated continuously. Figure 23-40 shows such a unit.

In the reactor shown in Fig. 23-41, a stable fluidized bed is maintained by recirculation of the mixed fluid through the bed and a draft tube. An external pump sometimes is used instead of the built-in impeller shown. Such units were developed for the liquefaction of coal and are called *ebullating beds.*

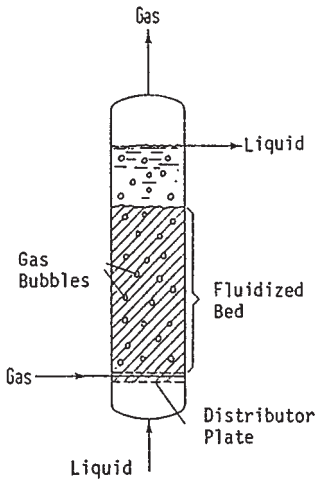


FIG. 23-40 Three-phase fluidized bed reactor.

Three-phase fluidized bed reactors are used for the treatment of heavy petroleum fractions at 350 to 600°C (662 to 1,112°F) and 200 atm (2,940 psi). A biological treatment process (Dorr-Oliver Hy-Flo) employs a vertical column filled with sand on which bacterial growth takes place while waste liquid and air are charged. A large interfacial area for reaction is provided, about 33 cm^2/cm^3 (84 in^2/in^3), so that an 85 to 90 percent BOD removal in 15 min is claimed compared with 6 to 8 h in conventional units.

TRICKLE BED PARAMETERS

Numerous studies have been made of the hydrodynamics and other aspects of the behavior of gas/liquid/solid systems, in particular of trickle beds, and including absorption and extraction in packed beds. Some of the literature is reviewed in the references at the end of this subsection.

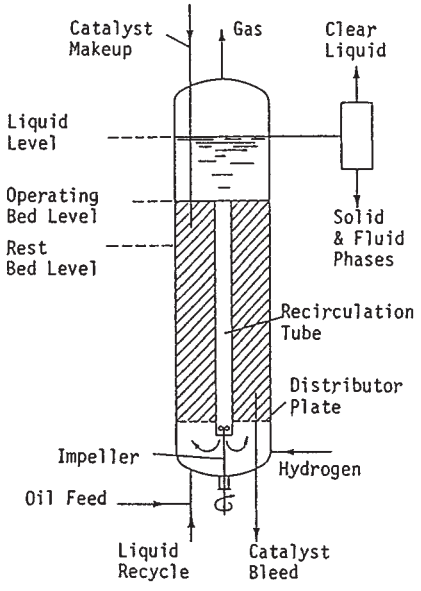


FIG. 23-41 Gas/liquid fluidized (ebullating) bed reactor for hydroliquefaction of coal. (*Kampiner, in Winnacker-Keuchler,* Chemische Technologie, *vol. 3, Hanser, 1972, p. 252.*)

Although many processes have progressed satisfactorily through the laboratory, pilot plant, and commercial scales, design from first principles and scale-up procedures have proved elusive. The various pieces of this puzzle that will be cited in this section, however, do tell us some of what is going on and should aid in the appraisal of the effects of changes in capacity and operating conditions of existing units.

Pressure Drop Some models regard trickle bed flow as analogous to gas/liquid flow in pipe lines. Various flow regimes may exist like those typified in Fig. 23-25*l* but in a vertical direction. The two-phase ΔP_{GL} is related to the pressure drops of the individual phases on the assumptions that they are flowing alone. The relation proposed by Larkin et al. (*AIChE Journal,* **7,** 231 [1961]) is

$$\ln \frac{\Delta P_{GL}}{\Delta P_L + \Delta P_G} = \frac{5.0784}{3.531 + (\ln X)^2}$$

$$X = \sqrt{\frac{\Delta P_L}{\Delta P_G}}, \qquad 0.05 \le X \le 30 \tag{23-109}$$

Several other correlations are cited in the literature, some of which agree with the one quoted here. Pressure drop usually is not a major factor in the design of a trickle bed.

Example 6: Conditions of a Trickle Bed A system has the properties of air/water at room conditions. Liquid is at 0.5 cm/s, gas at 10 cm/s, free volume fraction $\varepsilon_B = 0.4$, particle diameter $d_p = 0.5$ cm. The pressure drops by one of the many correlations for packed bed flow are $\Delta P_L = 217$, $\Delta P_G = 100$, so that $X = 1.47$ and $\Delta P_{GL} = 1{,}270$ N/m^3, Newtons/m^3 or 0.0124 atm/(m^2·m).

Liquid Holdup The major factor influencing this property is the liquid flow rate, but the shape, size, and wetting characteristics of the particles and the gas rate and the initial distribution of liquid also enter in. One of the simpler correlations is that of Midoux et al. (*J. Chem. Eng. Japan,* **9,** 350 [1976]).

$$\frac{\varepsilon_L}{\varepsilon_B} = \frac{0.66X^{0.81}}{1 + 0.66X^{0.81}}, \qquad 0.1 \le X \le 80 \tag{23-110}$$

where ε_B is the bed porosity. For Example 6 with $X = 1.47$ and $\varepsilon_B = 0.4$,

$$\varepsilon_L = 0.4(0.474) = 0.190$$

A correlation due to Sato (*J. Chem. Eng. Japan,* **6,** 147 [1973]) is

$$\frac{\varepsilon_L}{\varepsilon_B} = 0.185\left[\frac{6(1-\varepsilon_B)}{d_p}\right]^{1/3} X^{0.22} = 0.3659 \tag{23-111}$$

for the same example. There are also correlations for the static holdup; that is, when the flow rate is zero after wetting. For nonporous catalysts, usually $\varepsilon_{static} < 0.05$.

Gas/Liquid Mass Transfer This topic has been widely investigated for gas absorption in packed beds, usually countercurrent. One correlation for cocurrent flow in catalyst beds is by Sato et al. (*First Pacific Chemical Engineering Congress,* Pergamon, 1972, p. 187):

$$k_L a_B = 6.185(10^{-3}) d_p^{-0.5} u_L^{0.8} u_G^{0.8}, \qquad 1/\text{s}$$

For Example 6, this gives $k_L a_B = 8.8(10^{-3})$/s.

Gas/Liquid Interfacial Area This has been evaluated by measuring absorption rates like those of CO_2 in NaOH. A correlation by Charpentier (*Chem. Eng. Journal,* **11,** 161 [1976]) is

$$\frac{a_B}{a_p(1-\varepsilon_B)} = 0.05\left[\frac{\Delta P_{GL}\varepsilon_B}{a_p(1-\varepsilon_B)}\right]^{1.2} \tag{23-112}$$

With $a_p = 6/d_p = 1{,}200$/m, $\varepsilon_B = 0.4$, and $\Delta P_{GL} = 1{,}260$ N/m^3,

$$a_B = 0.05(1{,}200)(0.6)\left[\frac{1{,}260(2/3)}{1{,}200}\right]^{1.2} = 23.5 \text{ m}^2/\text{m}^3$$

For comparison, the geometrical area of the particles is

$$a_{geom} = \frac{6(1-\varepsilon_B)}{d_p} = \frac{6(0.6)}{0.005} = 72 \text{ m}^2/\text{m}^3$$

Liquid/Solid Mass Transfer The dissolved gas and the solvent react in contact with the surface of the catalyst. For studying the rate of transfer to the surface, an often-used system was benzoic acid or naphthalene in contact with water. A correlation of Dharwadkar and Sylvester (*AIChE Journal,* **23,** 376 [1977]) that agrees well with some others is

$$k_s = 1.637 u_L \text{Re}_L^{-0.331}\left(\frac{\rho_L D}{\mu_L}\right)^{2/3} \tag{23-113}$$

For the example with diffusivity of oxygen $D = 2.1(10^{-5})$ cm^2/s,

$$k_s = 1.637(0.1)\left[\frac{0.5(0.1)(1)}{0.01}\right]^{-0.331}\left[\frac{1(2.1)(10^{-5})}{0.01}\right]^{2/3}$$

$$= 1.7(10^{-3}) \text{ cm/s}$$

Axial Dispersion and the Peclet Number Peclet numbers are measures of deviation from plug flow. They may be calculated from residence time distributions found by tracer tests. Their values in trickle beds are ⅓ to ⅙ those of flow of liquid alone at the same Reynolds numbers. A correlation by Michell and Furzer (*Chem. Eng. J.,* **4,** 53 [1972]) is

$$\text{Pe}_L = \frac{u_L d_p}{D_{EL}} = \left(\frac{\text{Re}_L}{\varepsilon_L}\right)^{0.7}\left(\frac{\mu_L^2}{d_p^3 g \rho_L^2}\right)^{0.32} \tag{23-114}$$

where D_{EL} is the axial dispersion coefficient of the liquid, cm^2/s. In the range of Re = 10 to 100, the Peclet number is in the range 0.2 to 0.6 cm^2/s (0.03 to 0.09 in^2/s). It is insensitive to the kind of packing and to the gas flow. Gas-phase dispersions also have been measured and found to be one or two orders of magnitude less than in single-phase gas flows.

Plug flow is approached at low values of the dispersion coefficient or high values of Peclet number. A criterion developed by Mears (*Chem. Eng. Sci.,* **26,** 1361 [1971]) is that conversion will be within 5 percent of that predicted by plug flow when

$$\text{Pe} = \frac{u_L L}{D} > 20\, n \ln \frac{1}{1 - x_B} \tag{23-115}$$

where n is the order of the reaction with respect to B and x_B is the fractional conversion of B. For instance, when $L = 100$ cm, $n = 1$, $u_L = 0.8$ cm/s, and $x_B = 0.96$, then $D = 1.25$ cm^2/s. Note that the Pe numbers of the last two equations do not have the same linear term.

References for Gas/Liquid/Solid Reactions

de Lasa, H. I., *Chemical Reactor Design and Technology,* Martinus Nijhoff, 1986. Gianetto, A., and P. L. Silveston, eds., *Multiphase Chemical Reactors,* Hemisphere, 1986. Ramachandran, P. A., and R. V. Chaudhari, *Three-Phase Chemical Reactors,* Gordon & Breach, 1983. Rodrigues, A. E. et al., eds., *Multiphase Chemical Reactors,* vol. 2, Sijthoff & Noordhoff, 1981. Satterfield, C. N., "Trickle Bed Reactors," *AIChE Journal,* **21,** 209–228 (1975). Shah, Y. T., *Gas-Liquid-Solid Reactor Design,* McGraw-Hill, 1979.

REACTIONS OF SOLIDS

Many reactions of solids are industrially feasible only at elevated temperatures which are often obtained by contact with combustion gases, particularly when the reaction is done on a large scale. A product of reaction also is often a gas that must diffuse away from a remaining solid, sometimes through a solid product. Thus, thermal and mass-transfer resistances are major factors in the performance of solid reactions.

There are a number of commercial operations where the object is to make useful products with solid reactions. Design and practice, however, do not appear to rely generally on sophisticated kinetics, and they are rarely divulged completely. The desirable information is about temperatures, configuration, quality of mixing, and residence times or space velocities. Most of the information about current practice of reactions of solids is proprietary. Some of the sparse published data can

be cited. Scientific data for solid reactions are abundant but not very coherent. The same data can be fitted, equally badly, by several models. Nevertheless, quotation of some of those kinetic and mechanistic conclusions from the literature may throw some light on these processes. Some data for reactions of solids are shown in Fig. 23-42.

THERMAL DECOMPOSITIONS

All substances are unstable above certain temperatures. The main theory of the rates of decomposition of solids is that they begin at positions of strain on the surface, called *nuclei* or *active sites;* as the reaction progresses, the number of nuclei and their sizes grow. In accordance with this theory the conversion varies as some power of the time, that is, as t^n, where n commonly assumes a value of 3 to 6 but the range is from about 1 to 8. Other rate expressions also have been fitted to certain results. Activation energies represented by the Arrhenius equation sometimes change during the course of a reaction, indicating a change of mechanism.

Decompositions may be exothermic or endothermic. Solids that decompose without melting upon heating are mostly such that can give rise to gaseous products. When a gas is made, the rate can be affected by the diffusional resistance of the product zone. Particle size is a factor. Aging of a solid can result in crystallization of the surface that has been found to affect the rate of reaction. Annealing reduces strains and slows any decomposition rates. The decompositions of some fine powders follow a first-order law. In other cases, the decomposed fraction x is in accordance with the Avrami-Erofeyev equation (cited by Galwey, *Chemistry of Solids,* Chapman Hall, 1967)

$$-\ln (1 - x) = kt^n \tag{23-116}$$

with n = 3.5 to 4. Another rule of simple form also cited by Galwey that sometimes applies is

$$x = k(t - t_1)^n \tag{23-117}$$

with n as great as 6. The equation of Prout and Tompkins is of autocatalytic form,

$$\frac{dx}{dt} = kx(1 - x), \qquad \ln \frac{x}{1 - x} = kt + C \tag{23-118}$$

It states that the rate is proportional to the fraction x that has decomposed (which is dominant early in the reaction) and to the fraction not decomposed (which is dominant in latter stages of reaction). The decomposition of potassium permanganate and some other solids is in accordance with this equation. The shape of the plot of x against t is sigmoid in many cases, with slow reactions at the beginning and end, but no theory has been proposed that explains everything.

Organic Solids A few organic compounds decompose before melting, mostly nitrogen compounds: azides, diazo compounds, and nitramines. The processes are exothermic, classed as explosions, and may follow an autocatalytic law. Temperature ranges of decomposition are mostly 100 to 200°C (212 to 392°F). Only spotty results have been obtained, with no coherent pattern. The decomposition of malonic acid has been measured for both the solid and the supercooled liquid. The first-order specific rates at 126.3°C (259.3°F) were 0.00025/min for solid and 0.00207 for liquid, a ratio of 8; at 110.8°C (231.4°F), the values were 0.000021 and 0.00047, a ratio of 39. The decomposition of oxalic acid (m.p. 189°C) obeyed a zero-order law at 130 to 170°C (266 to 338°F).

Exothermic Decompositions These decompositions are nearly always irreversible. Solids with such behavior include oxygen-containing salts and such nitrogen compounds as azides and metal styphnates. When several gaseous products are formed, reversal would require an unlikely complex of reactions. Commercial interest in such materials is more in their storage properties than as a source of desirable products, although ammonium nitrate is an important explosive. A few typical examples will be cited to indicate the ranges of reaction conditions. They are taken from the review by Brown et al. ("Reactions in the Solid State," in Bamford and Tipper, *Comprehensive Chemical Kinetics,* vol. 22, Elsevier, 1980).

Silver oxalate decomposes smoothly and completely in the range 100 to 160°C (212 to 320°F). One investigation showed $x = k(t - t_1)^n$ with n = 3.5 to 4, and an activation energy of 27 kcal/g mol (48,600 Btu/lb mol).

Ammonium chromates and some other solids exhibit aging effects. Material that has been stored for months or years follows a cubic law with respect to time, but fresh materials are about fifth-order. At 199°C (390°F), the Prout-Tompkins law was followed.

Ammonium nitrate decomposes into nitrous oxide and water. In the solid phase, decomposition begins at about 150°C (302°F) but becomes extensive only above the melting point (170°C) (338°F). The reaction is first-order, with activation energy about 40 kcal/g mol (72,000 Btu/lb mol). Traces of moisture and Cl^- lower the decomposition temperature; thoroughly dried material has been kept at 300°C (572°F). All oxides of nitrogen, as well as oxygen and nitrogen, have been detected in decompositions of nitrates.

Styphnic acid is a nitrogen compound. Lead styphnate monohydrate was found to detonate at 229°C (444°F), but the course of decomposition could be followed at 228°C and below.

Many investigations are reported on azides of barium, calcium, strontium, lead, copper, and silver in the range 100 to 200°C (212 to 392°F). Time exponents were 6 to 8 and activation energies of 30 to 50 kcal/g mol (54,000 to 90,000 Btu/lb mol) or so. Some difficulties with reproducibility were encountered with these hazardous materials.

Endothermic Decompositions These decompositions are mostly reversible. The most investigated substances have been hydrates and hydroxides, which give off water, and carbonates, which give off CO_2. Dehydration is analogous to evaporation, and its rate depends on the moisture content of the gas. Activation energies are nearly the same as reaction enthalpies. As the reaction proceeds in the particle, the rate of reaction is impeded by resistance to diffusion of the water through the already formed product. A particular substance may have several hydrates. Which one is present will depend on the partial pressure of water vapor in contact. $FeCl_2$, for instance, combines with 4, 5, 7, or 12 molecules of water with melting points ranging from about 75 to 40°C (167 to 104°F).

Dehydration of $CuSO_4$ pentahydrate at 53 to 63°C (127 to 145°F) and of the trihydrate at 70 to 86°C (158 to 187°F) obey the Avrami-Erofeyev equation. The rate of water loss from $Mg(OH)_2$ at lower temperatures is sensitive to partial pressure of water. Its decomposition above 297°C (567°F) yields appreciable amounts of hydrogen and is not reversible.

Carbonates decompose at relatively high temperatures, 660 to 740°C (1,220 to 1,364°F) for $CaCO_3$. When large samples are used the rate of decomposition can be controlled by the rate of heat transfer or the rate of CO_2 removal.

Some ammonium salts decompose reversibly with release of ammonia, for example,

$$(NH_4)_2SO_4 \Leftrightarrow NH_4HSO_4 + NH_3$$

at 250°C (482°F). Further heating can release SO_3 irreversibly.

The decomposition of silver oxide was one of the earliest solid reactions studied. It is smoothly reversible below 200°C (392°F) with equation for partial pressure of oxygen,

$$\frac{dp}{dt} = k\left(\frac{1 - p}{p_{\text{equilib}}}\right)$$

The reaction is sensitive to the presence of metallic silver at the start, indicating autocatalysis, and to the presence of silver carbonate, which was accidentally present in some investigations.

SOLID REACTION EXAMPLES

Diffusion of ions or molecules in solids is preliminary to reaction. It takes place through the normal crystal lattices of reactants and products as well as in channels and fissures of imperfect crystals. It is slow in comparison with that in fluids even at the elevated temperatures at which such reactions have to be conducted. In cement manufacture, for instance, reaction times are 2 to 3 h at 1,200 to 1,500°C (2,192 to 2,732°F) even with 200-mesh particles.

Large contact areas between solid phases are essential. For experimental purposes they are enhanced by forming and mixing fine powders and compressing them. The practices of powder metallurgy are

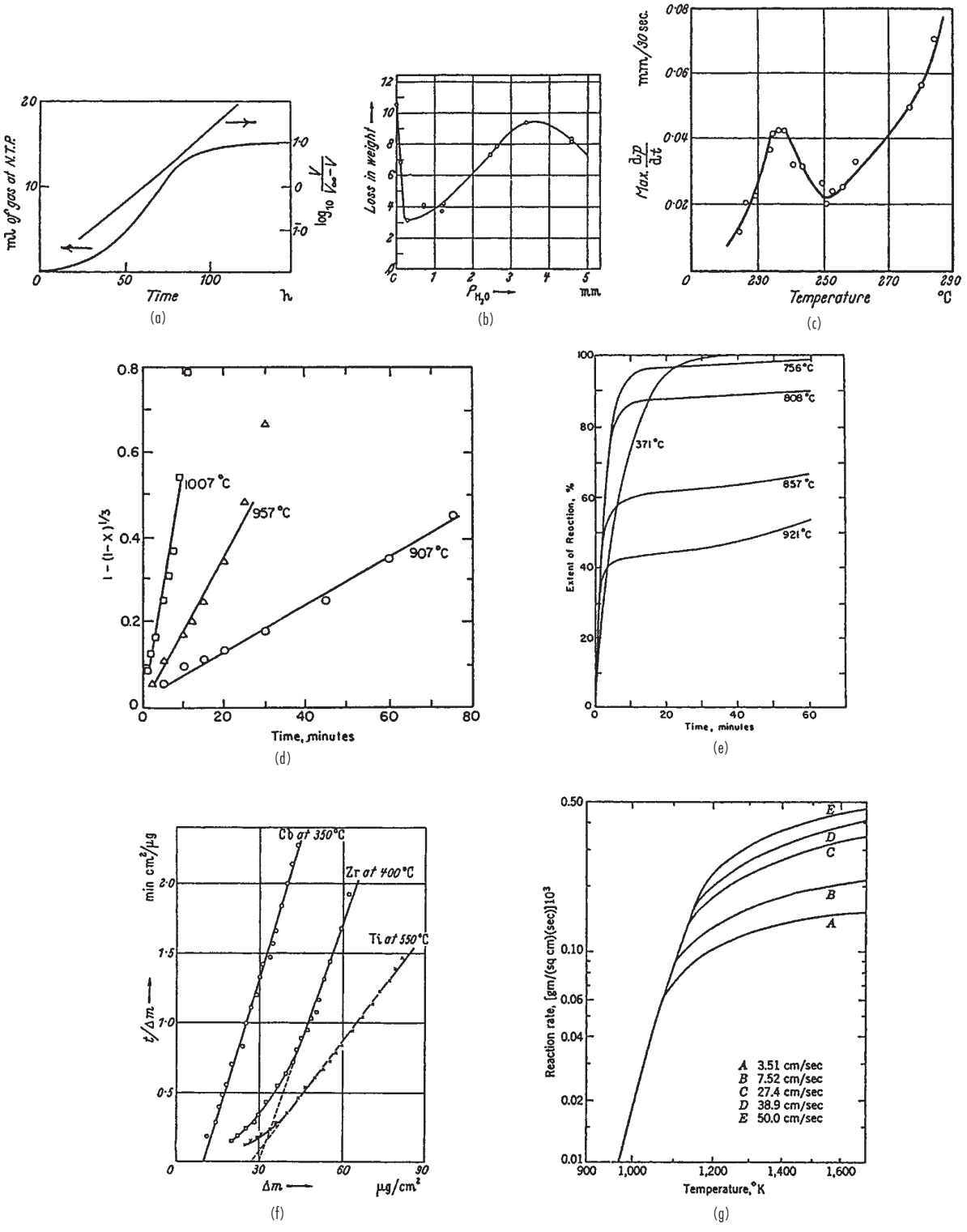


FIG. 23-42 Data for reactions of solids. (*a*) Thermal decomposition of 2-nitrobenzene-4-diazo-1 oxide at 99.1°C (*Vaughan and Williams,* J. Chem. Soc., *p. 1,560* [*1946*]). (*b*) Decomposition of $CuSO_4 \cdot 5H_2O$; the first four molecules are removed easily, the last with difficulty (*Kohlschutter and Nitschmann, 1931*). (*c*) Decomposition of ammonium perchlorate (*Bircumshaw and Newman,* Proc. Roy. Soc., ***A227,*** *228* [*1955*]). (*d*) Reduction of hematite by graphite in the presence of lithium oxide catalyst (*Rao,* Met. Trans., **2,** *1439* [*1971*]). (*e*) Reduction of nickel oxide by hydrogen; sintering begins just above 750°C (*Hashimoto and Silveston,* AIChE Journal, ***19,*** *268* [*1973*]). (*f*) Oxidation of metals, examples of parabolic law, with rate inversely proportional to the weight gain (*Gulbransen and Andrew,* Trans. Electrochem. Soc., ***96,*** *364* [*1949*]). (*g*) Effect of air velocity on combustion of carbon (*Tu et al.,* Ind. Eng. Chem., **26,** *749* [*1934*]).

examples, where particles are 0.1 to 1,000 μm and pressures are 138 to 827 MPa (20,000 to 60,000 psi). Apart from research laboratories, reactions of solids occur in ceramic, metallurgical, and other technologies. Commercial processes of this category include:

- Cement manufacturing
- Boron carbide from boron oxide and carbon
- Calcium silicate from lime and silica
- Calcium carbide by reaction of lime and carbon
- Leblanc soda ash

A limited number of laboratory results of varied nature will be cited for perspective. The mechanism of formation of zinc ferrite,

$$ZnO + Fe_2O_3 \Rightarrow ZnFe_2O_4$$

has been extensively studied at up to 1,200°C (2,192°F). At some lower temperatures the ZnO is the mobile phase and migrates to coat the Fe_2O_3 particles. In the reaction $MgO + Fe_2O_3 \Rightarrow MgFe_2O_4$, the MgO likewise is the mobile phase. There, smaller particles (<1 μm) obeyed the power law $x = k \ln t$, but larger ones had a more complex behavior. In the reaction

$$2AgI + HgI_2 \Rightarrow Ag_2HgI_4$$

nearly equivalent amounts of the ions Ag^+ and Hg^{2+} migrating in opposite directions arrived at their respective interfaces after 66 days at 65°C (149°F).

For the reaction $KClO_4 + 2C \Rightarrow KCl + CO_2$, fine powders were compressed to 69 MPa (10,000 psi) and reacted at 350°C (662°F), well below the 500°C (932°F) melting point. The kinetic data were fitted by the equation

$$\frac{dx}{dt} = k(a-x)^{2/3}x^{-1/3}$$

The term $(a-x)^{2/3}$ was included as a measure of the surface area of the oxidizing salt and the $x^{-1/3}$ term is associated with the reduction of contact area from product formation.

Several other reactions that yield gaseous products have attracted investigators because their progress is easily followed, for instance,

$$MnO_3 + 2MoO_3 \Rightarrow 2MnMoO_4 + 0.5O_2$$

where MoO_3 was identified as the mobile phase, and

$$Ca_3(PO_4)_2 + 5C \Rightarrow 3CaO + P_2 + 5CO$$

which obeyed the equation

$$-\ln(1-x) = kt$$

The reaction

$$CuCr_2O_4 + CuO \Rightarrow Cu_2Cr_2O_4 + 0.5O_2$$

eventually becomes diffusion-controlled and becomes described by

$$[1-(1-x)^{1/3}]^2 = k \ln t$$

In the case where two solid products are formed,

$$CsCl + NaI \Rightarrow CsI + NaCl$$

the rate-controlling step is the diffusion of iodide ion in CsCl.

The kinetic equation can vary with a number of factors. For the reaction between tricalcium phosphate and urea, relatively coarse material (−180+200 mesh) obeyed the law $x^2 = kt$ with $E = 18$ kcal/g mol (32,400 Btu/lb mol) and finer material (−300+320 mesh) obeyed a first-order equation with $E = 28$ kcal/g mol.

Carbothermic Reactions Some apparently solid/solid reactions with carbon apparently take place through intermediate CO and CO_2. The reduction of iron oxides has the mechanism

$$Fe_xO_y + yCO \Rightarrow xFe + yCO_2, \qquad CO_2 + C \Rightarrow 2CO$$

Some results of the reduction of hematite by graphite at 907 to 1,007°C in the presence of lithium oxide catalyst were correlated by the equation $1-(1-x)^{1/3} = kt$. The reaction of solids ilmenite and carbon has the mechanism

$$FeTiO_3 + CO \Rightarrow Fe + TiO_2 + CO_2, \qquad CO_2 + C \Rightarrow 2CO$$

and that between chromium oxide and chromium carbide,

$$\frac{1}{6}Cr_{23}O_6 + CO_2 \Rightarrow \frac{23}{6}Cr + 2CO, \qquad \frac{1}{3}Cr_2O_3 + CO \Rightarrow \frac{2}{3}Cr + CO_2$$

A similar case is the preparation of metal carbides from metal and carbon,

$$C + 2H_2 \Rightarrow CH_4, \qquad Me + CH_4 \Rightarrow MeC + 2H_2$$

SOLIDS AND GASES

Commercial processes of solid/gas reactions include:

- Oxidation with air of sulfides in ores to oxides or sulfates that are more easily processed for metal recovery.
- Conversion of Fe_2O_3 to magnetic Fe_3O_4 in contact with reducing atmosphere of CO in combustion gases.
- Chlorination of ores of uranium, titanium, zirconium and aluminum. For titanium, carbon also is needed:

$$TiO_2 + C + 2Cl_2 \Rightarrow TiCl_4 + CO_2$$

- Manufacture of hydrogen by action of steam on iron.
- Manufacture of blue gas by action of steam on carbon.
- Calcium cyanamide by action of atmospheric nitrogen on calcium carbide.
- Nitriding of steel.
- Atmospheric corrosion.
- Combustion of solid fuels.

A classification of processes can be made with respect to the nature of the reaction product, as follows:

1. The product is a gas, as in the reaction between finely divided nickel and CO which makes nickel carbonyl, boiling point 42°C.
2. The product is a loose solid that offers no appreciable diffusional resistance to the gas reactant.
3. The product is an adherent solid that may or may not be permeable to the gas reactant.
4. The reacting solid is in granular form. Decrease in the area of the reaction interface occurs as the reaction proceeds. The mathematical modeling is distinguished from that with flat surfaces, which are most often used in experimentation.

Literature A number of informative researches can be cited, but again the difficulties of experimentation and complicating factors have made the kinetic patterns difficult to generalize. The most investigated gas reactants have been oxygen and hydrogen and some chlorine systems.

When the product of reaction does not prove a barrier to further chemical change, the rate is constant, zero-order, and the weight of product is proportional to time,

$$w = kt$$

Such behavior is observed with alkali and alkaline earth oxidations where the oxide volume is less than the metal volume and cracks develop in the product coat, permitting ready access for further reaction.

Oxide films of Al and Cr, for instance, are protective beyond a small amount of reaction, since they are nonporous and adherent.

When the product layer is porous the reaction will continue but at decreasing rate as the diffusional resistance increases with increasing conversion. Then,

$$\frac{dw}{dt} = \frac{k}{w}$$

This rate expression is known as the *parabolic law*. It is obeyed by oxidation of Ni, Ti, Cu, and Cr and by halogenation of silver. The product coat retards both diffusion and heat transfer.

The behavior type may change with temperature range. For instance, oxidation of zinc above 350°C (662°F) obeys the parabolic law, but at lower temperature the product coat seems to develop cracks and the *logarithmic law*, $\ln w = kt$, is observed.

One mathematical model of the oxidation of nickel spheres was confirmed when it took into account the decrease in the reaction surface as the reaction proceeded.

EQUIPMENT AND PROCESSES

Reactions of solids of commercial interest almost always involve a gas as a reagent and/or a heat source. Some of the equipment in use is represented in Fig. 23-43. Temperatures are usually high so the

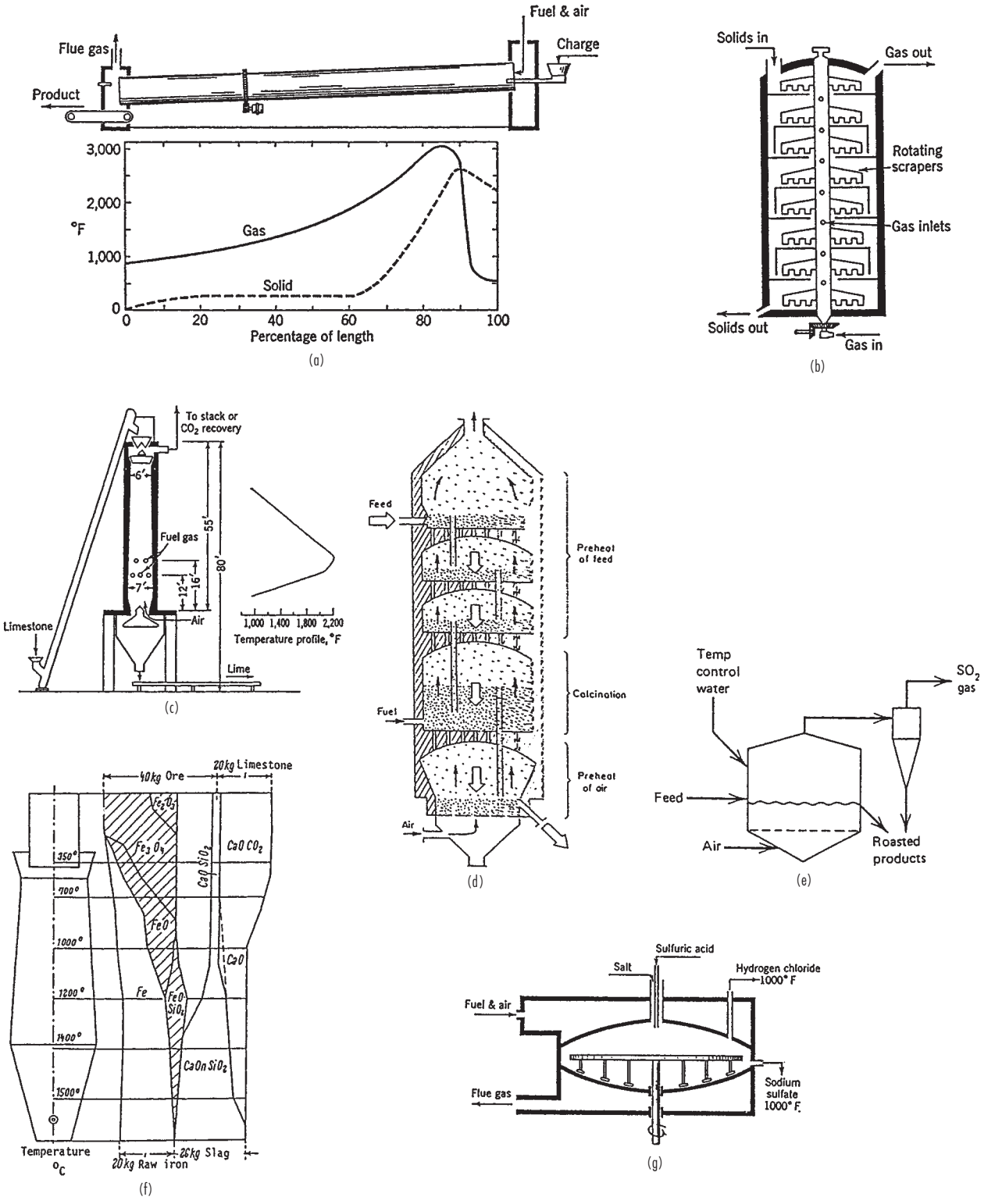


FIG. 23-43 Reactors for solids. (*a*) Temperature profiles in a rotary cement kiln. (*b*) A multiple hearth reactor. (*c*) Vertical kiln for lime burning, 55 ton/d. (*d*) Five-stage fluidized bed lime burner, 4 by 14 m, 100 ton/d. (*e*) A fluidized bed for roasting iron sulfides. (*f*) Conditions in a vertical moving bed (blast furnace) for reduction of iron oxides. (*g*) A mechanical salt cake furnace. To convert ton/d to kg/h, multiply by 907.

equipment is mostly refractory-lined. The solid is in granular form, at most a few mm or cm in diameter. Historically, much of the equipment was developed for the treatment of ores and the recovery of metals. More than 50 processes for reduction of iron ores, for instance, have been developed, although the clear winner is the blast furnace. This is a vertical moving-bed device; iron oxides and coal are charged at the top and flow countercurrently to combustion and reducing gases. Units of 1,080 to 4,500 m^3 (38,000 to 159,000 ft^3) may produce up to 9×10^6 kg (20×10^6 lbm) of molten iron per day. Figure 23-43*f* identifies the temperature and composition profiles (Blom, Stahl, and Eisen, **47,** 955 [1927]). Reduction is with CO and H_2 that are made from coal, air, and water within the reactor.

Pyrometallurgical Processes Such high temperature processes convert certain minerals into others for easier separation from gangue or for easier recovery of metal. They are accomplished in kilns, hearth furnaces or fluidized bed reactors.

Oxidation Proceeds according to the stoichiometry $MeS + 1.5O_2 \Rightarrow MeO + CO_2$. Applied to Fe, Pb, Cu, and Ni.

Calcining Proceeds according to $MeCO_3 \Rightarrow MeO + CO_2$. Applied to Ca, Mg, and Ba.

Sulfating $MeS + 2O_2 \Rightarrow MeSO_4$. Applied to Cu, of which the sulfate is water-soluble.

Chlorination $MeO + Cl_2 + C \Rightarrow MeCl_2 + CO$. Applied to Mg, Be, Ti, and Zr, whose chlorides are water-soluble. The chlorine can be supplied indirectly, as in $Cu_2S + 2NaCl + O_2 \Rightarrow 2CuCl + Na_2SO_4$.

Reduction $MeO + H_2 \Rightarrow Me + H_2O$, $MeO + CO \Rightarrow Me + CO_2$. Applied to Fe, W, Mo, Ge, and Zn.

Magnetic Roasting $Fe_2O_3 + CO \Rightarrow Fe_3O_4$. Recovered magnetically.

Rotary Kiln Equipment A rotary kiln is a long, narrow cylinder inclined 2 to 5 degrees to the horizontal and rotated at 0.25 to 5 rpm. It is used for the decomposition of individual solids, for reactions between finely divided solids, and for reactions of solids with gases or even with liquids. The length/diameter ratio ranges from 10 to 35, depending on the reaction time needed. The solid is in granular form and may have solid fuel mixed in. The granules are scooped into the vapor space and are heated as they cascade downwards. Holdup of solids is 8 to 15 percent of the cross section. For most free-falling materials, the solids pattern approaches plug flow axially and complete mixing laterally. Rotary kilns can tolerate some softening and partial fusion of the stock.

Approximate ranges of space velocities in rotary kilns, metric tons/(m^3·d), of selected processes are as follows:

Cement, dry process	0.4–1.1
Cement, wet process	0.4–0.8
Cement, with heat exchange	0.6–1.8
Lime burning	0.5–0.9
Dolomite burning	0.4–0.6
Pyrite roasting	0.2–0.35
Clay calcination	0.5–0.8
Magnetic roasting	1.5–2.0
Ignition of inorganic pigments	0.15–2.0
Barium sulfide preparation	0.35–0.8

Formulas for capacity and residence time in terms of operating conditions are due to Heiligenstaedt:

$$W = 148 n \phi D^3 \tan \vartheta, \qquad \text{t/(m}^3\text{·d)} \qquad (23\text{-}119)$$

$$\tau = \frac{L}{60 \pi n D \tan \vartheta}, \qquad \text{h} \qquad (23\text{-}120)$$

where n = rpm
ϕ = fraction of cross section occupied
D = diameter, m
L = length, m
ϑ = degrees inclination to the horizontal

High-temperature heat transfer from the gas is by radiation and convection.

Vertical Kilns These kilns are used primarily where no fusion or softening occurs, as in the burning of limestone or dolomite, although rotary kilns also are used for these operations. The blast furnace, Fig. 23-43*f*, is a vertical kiln in which fusion takes place in the lower section. A cross section of a continuous lime kiln is shown in Fig. 23-43*c* which is for 50,000 kg/day (110,000 lbm/d). The diameter range of these kilns is 2.4 to 4.5 m (7.9 to 14.8 ft) and height 15 to 24 m (49 to 79 ft). Peak temperatures in lime calcination are 1,200°C (2,192°F), although decomposition proceeds freely at 1,000°C (1,832°F). Fuel supply may be coke mixed and fed with the limestone or other fuel. Space velocity of the kiln is 14 to 25 kg CaO/(m^3·h) (0.87 to 1.56 lbm/[ft^2·h]) or 215 to 485 kg CaO/(m^2·h) (44 to 99 lbm/[ft^2·h]), depending on the size and modernity of the kiln, the method of firing, and the lump size, which is in the range of 10 to 25 cm (3.9 to 9.8 in). A five-stage fluidized bed calciner is sketched in Fig. 23-43*d*. Such a unit 4 m (13 ft) in diameter and 14 m (46 ft) high has a production of 91,000 kg CaO/d (200,000 lbm/d).

Cement Manufacture Kilns These kilns are up to 6 m (17 ft) in diameter and 200 m (656 ft) long. Inclination is 3 to 4 degrees, and rotation is 1.2 to 2.0 rpm. Typical temperature profiles are shown in Fig. 23-43*a*. Near the flame the temperature is 1,800 to 2,000°C (3272 to 3632°F). The temperature of the solid reaches 1,350 to 1,500°C (2,462 to 2,732°F) which is necessary for clinker formation. In one smaller kiln, a length of 23 m (75 ft) was allowed for drying, 34 m (112 ft) for preheating, 19 m (62 ft) for calcining, and 15 m (49 ft) for clinkering. Total residence time is 40 min to 5 h, depending on the type of kiln. The time near the clinkering temperature of 1,500°C (2,732°F) is 10 to 20 min. Subsequent cooling is as rapid as possible.

A kiln 6 m (20 ft) in diameter by 200 m (656 ft) can produce 2.7×10^6 kg/d (6×10^6 lbm/d) of cement. For production rates less than 270,000 kg/d (600,000 lbm/d), shaft kilns are used. These are vertical cylinders 2 to 3 m (6.5–10 ft) by 8 to 10 m (26–33 ft) high, fed with raw meal pellets and finely ground coal.

Roasting of Sulfide Ores In this process iron sulfide (pyrite) is burned with air for recovery of sulfur and to make the iron oxide from which the metal is more easily recovered. Sulfides of other metals also are roasted. The original kind of equipment was a multiple hearth furnace, as shown in Fig. 23-43*b*. In some designs the plates rotate, in others the scraper arms rotate, and in still others the arms oscillate and discharge the material to lower plates at each stroke. Material is charged at the top, moves along as the rotation proceeds, and drops onto successively lower plates while combustion gases or gaseous reactants flow upward. A reactor with 9 trays 5 m (16 ft) in diameter and 12 m (39 ft) high can roast about 600 kg/h (1,300 lbm/h) of pyrite. Another unit with 11 trays 2 m (7 ft) in diameter is said to have a capacity of 114,000 kg/d (250,000 lbm/d).

A major portion of the reaction is found to occur in the vapor space between trays. A unit in which most of the trays are replaced by empty space is called a *flash roaster;* its mode of operation is like that of a spray dryer.

Molybdenum sulfide is roasted at the rate of 5500 kg/d (12,000 lbm/d) in a unit with 9 stages, 5 m (16 ft) diameter, at 630 ± 15°C (1,166 ± 27°F), sulfur going from 35.7 percent to 0.04 to 0.006 percent.

A Dorr-Oliver fluidized bed roaster 5.5 m (18 ft) in diameter, 7.6 m (25 ft) high, with a bed height of 1.2 to 1.5 m (3.9 to 4.9 ft) has a capacity of 154,000 to 200,000 kg/d (340,000–440,000 lbm/d) at 650 to 700°C (1,200 to 1,300°F) (Kunii and Levenspiel, *Fluidization Engineering,* Butterworth, 1991). Two modes of operation can be used for a fluidized bed unit like that shown in Fig. 23-43*e*. In one operation, a stable bed level is maintained at a superficial gas velocity of 0.48 m/s (1.6 ft/s); a unit 4.8 m (16 ft) in diameter, 1.5 m (4.9 ft) bed depth, 3 m (9.8 ft) freeboard, has a capacity of 82,000 kg/d (180,000 lbm/d) pyrrhotite, 200 mesh, 53 percent entrained solids, 875°C (1,600°F). In the other mode, the superficial gas velocity is 1.1 m/s (3.6 ft/s) and 100 percent entrainment occurs. This is called *transfer line* or *pneumatic transport reaction;* a unit 6.6 m (22 ft) diameter by 1.8 m (5.9 ft) handles 545,000 kg/d (1.2×10^6 lbm/d), 200 mesh, 780°C (1,436°F).

Magnetic Roasting In this process ores containing Fe_2O_3 are reduced with CO to Fe_3O_4, which is magnetically separable from gangue. Rotary kilns are used, temperatures 700 to 800°C (1,292 to 1,472°F). Higher temperatures form FeO. A reducing-gas atmosphere is created by firing a deficiency of air with carbonaceous fuels. Data for two installations are as follows.

Measurements	Charge, t/d	Product, t/d
3.6 by 44 m	900–960, 21% Fe	350–368, 41–42% Fe
3.6 by 50 m	1,300	—

A unit for 2.3×10^6 kg/d (5×10^6 lbm/d) has a power consumption of 0.0033 to 0.0044 kwh/kg (3 to 4 kwh/ton) and a heat requirement of 180,000 to 250,000 kcal/ton (714,000 to 991,000 Btu/ton). The magnetic concentrate can be agglomerated for further treatment by pelletizing or sintering.

Sodium Sulfate A single-hearth furnace is used, like that shown in Fig. 23-40*g*. Sodium chloride and sulfuric acid are charged continuously to the center of the pan and the rotating scrapers gradually work the reacting mass to the periphery, where the sodium sulfate is discharged at 540°C (1,000°F). Pans are 3.3 to 5.5 m (11 to 18 ft) in diameter and can handle 5,500 to 9,000 kg/d (12,000 to 20,000 lbm/d) of salt. Rotary kilns also are used for this purpose. Such a unit 1.5 m (4.9 ft) in diameter by 6.7 m (22 ft) has a capacity of 22,000 kg/d (48,000 lbm/d) of salt cake. A pan furnace also is used, for instance, in the Leblanc soda ash process and for making sodium sulfide from sodium sulfate and coal.

Desulfurization with Dry Lime Limestone or lime or dolomite ($CaCO_3 \cdot MgCO_3$) in a fluidized bed coal combustor reacts with SO_2 in the gas to make $CaSO_4$. The most favorable conditions with lime are 1 atm (14.7 psi) and 800 to 850°C (1,472 to 1,562°F). At higher temperatures the sulfate tends to decomposition, according to $CaSO_4 + CO \Rightarrow CaO + CO_2 + SO_2$. Dolomite works better at 950°C (1,742°F) and 3 to 10 atm (44 to 147 psi). Although $MgSO_4$ is not formed, the pore structure with dolomite is more open to diffusion of SO_2. The pores of the CaO tend to be clogged by $CaSO_4$, but the attrition in a fluidized bed helps the extent of utilization of the lime which, at best, is only partial. A mol ratio Ca/S of 3 to 5 is needed to get as much as 70 to 80 percent removal of the sulfur. Reactivities of limestones are variable, depending on the content of impurities. Ground particle sizes are 1.5 to 5 mm (0.059 to 0.20 in), bed depths 1.2 to 3 m (3.9 to 9.8 ft), residence times of lime 0.5 to 2.5 s. The reaction seems to be first-order in SO_2. The solid $CaSO_4$ is a waste product. It is technically, although not economically, feasible to use it for making sulfuric acid.

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Section 24

Biochemical Engineering

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Nomenclature and Units

Symbol	Definition	SI units	U.S. customary units
A	Empirical constant	Dimensionless	Dimensionless
C	Concentration (mass)	kg/m^3	lb/ft^3
C	Concentration	mol/m^3	$(lb \cdot mol)/ft^3$
D	Diameter	m	ft
D	Effective diffusivity	m^2/s	ft^2/h
D	F/V	s^{-1}	h^{-1}
DRT	Decimal reduction time for sterilization	s	h
E	Activation energy	cal/mol	Btu/(lb·mol)
F	Flow or feed rate	m^3/s	ft^3/h
H	Concentration of host organisms	kg/m^3	lb/ft^3
K	Rate coefficient	Units dependent on order of reaction	Units dependent on order of reaction
K_M	Michaelis constant	kg/m^3	lb/ft^3
$K_l a$	Lumped mass-transfer coefficient	s^{-1}	h^{-1}
K_d	Death-rate coefficient	s^{-1}	h^{-1}
K_s	Monod coefficient	kg/m^3	lb/ft^3
k	Kinetic constants	Dependent on reaction order	Dependent on reaction order
M	Coefficient for maintenance energy	Dimensionless	Dimensionless
N	Numbers of organisms or spores	Dimensionless	Dimensionless
P	Product concentration	kg/m^3	lb/ft^3
Q_{O_2}	Specific-respiration-rate coefficient	kg O_2/(kg organism·s)	lb O_2/(lb organism·h)
R	Universal-gas-law constant	8314 J/(mol·K)	0.7299 (ft^3)(atm)/(lb·mol·R)
r	Radial position	m	ft
S	Substrate concentration	kg/m^3	lb/ft^3
S	Shear	N/m^2	lbf/ft^2
S_o	Substrate concentration in feed	kg/m^3	lb/ft^3
T	Temperature	K	°F
t	Time	s	h
V	Velocity of reaction	mol/s	(lb·mol)/h
V_m	Maximum velocity of reaction	mol/s	(lb·mol)/h
V	Air velocity	m/s	ft/h
V	Fermenter volume	m^3	ft^3
VVM	Volume of air/volume of fermentation broth per minute	Dimensionless	Dimensionless
X	Organism concentration	kg/m_3	lb/ft^3
Y	Yield coefficient	kg/kg	lb/lb
	Greek symbols		
β	Dimensionless Michaelis constant	Dimensionless	Dimensionless
μ	Specific-growth-rate coefficient	s^{-1}	h^{-1}
$\hat{\mu}$ or μ_{max}	Maximum-specific-growth-rate coefficient	s^{-1}	h^{-1}
ω	Recycle ratio	Dimensionless	Dimensionless
ϕ	Thiele modulus	Dimensionless	Dimensionless

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INTRODUCTION TO BIOCHEMICAL ENGINEERING

The differences between biochemical engineering and chemical engineering lie not in the principles of unit operations and unit processes but in the nature of living systems. The commercial exploitation of cells or enzymes taken from cells is restricted to conditions at which these systems can function. Most plant and animal cells live at moderate temperatures and do not tolerate extremes of pH. The vast majority of microorganisms also prefer mild conditions, but some thrive at temperatures above the boiling point of water or at pH values far from neutrality. Some can endure concentrations of chemicals that most other cells find highly toxic. Commercial operations depend on having the correct organisms or enzymes and preventing inactivation or the entry of foreign organisms that could harm the process.

The pH, temperature, redox potential, and nutrient medium may favor certain organisms and discourage the growth of others. For example, pickles are produced in vats by lactobacilli well-suited to the acid conditions and with small probability of contamination by other organisms. In mixed culture systems, especially those for biological waste treatment, there is an ever shifting interplay between microbial populations and their environments that influences performance and control. Although open systems may be suitable for hardy organisms or for processes in which the conditions select the appropriate culture, many bioprocesses are closed and have elaborate precautions to prevent contamination. The optimization of the complicated biochemical activities of isolated strains, of aggregated cells, of mixed populations, and of cell-free enzymes or components presents engineering challenges that are sophisticated and difficult. Performance of a bioprocess can suffer from changes in any of the many biochemical steps functioning in concert, and genetic controls are subject to mutation. Offspring of specialized mutants that yield high concentrations of product tend to revert during propagation to less productive strains—a phenomenon called *rundown.*

This section emphasizes cell cultures and microbial and enzymatic processes and excludes medical, animal, and agricultural engineering systems. Engineering aspects of biological waste treatment are covered in Sec. 25.

Biotechnology has a long history—fermented beverages have been produced for several thousand years. But biochemical engineering is not yet fully mature. Developments such as immobilized enzymes and cells have been exploited partially, and many exciting advances should be forthcoming. Genetic manipulations through recombinant DNA techniques are leading to practical processes for molecules that could previously be found only in trace quantities in plants or animals. Biotechnology is now viewed as a highly profitable route to relatively valuable products. In the near future, costs of environmental protection may force more companies to switch from chemical processing that generates wastes that are costly to treat to biochemical methods with wastes that are easily broken down by biological waste treatment processes and that present much less danger to the environment. Some commercial bioprocesses could have municipal and industrial wastes as feedstocks, and the credits for accepting them should improve the economic prospects. When petroleum runs out and the

prices soar for petrochemicals, there will be large profits for fermentations that produce equivalent compounds.

BIOLOGICAL CONCEPTS

Cells The cell is the unit of life. Cells in multicellular organisms function in association with other specialized cells, but many organisms are free-living single cells. Although differing in size, shape, and functions, there are basic common features in all cells. Every cell contains cytoplasm, a colloidal system of large biochemicals in a complex solution of smaller organic molecules and inorganic salts. The cytoplasm is bounded by a semielastic, selectively permeable cell membrane that controls the transport of molecules into and out of the cell. There are biochemical transport mechanisms that spend energy to bring substances into the cell despite unfavorable concentration gradients across the membrane. Cells are protected by rigid cell walls external to the cell membranes. Certain bacteria, algae, and protozoa have gelatinous sheaths of inorganic materials such as silica.

Sequences of genes along a threadlike chromosome encode information that controls cellular activity. As units of heredity, genes determine the cellular characteristics passed from one generation to the next. In most cells, the chromosomes are surrounded by a membrane to form a conspicuous nucleus. Cells with organized nuclei are described as eukaryotic. Other intracellular structures serve as specialized sites for cellular activities. For example, photosynthesis is carried out by organelles called chloroplasts. In bacteria and cyanobacteria (formerly called blue-green algae), the chromosomes are not surrounded by a membrane, and there is little apparent subcellular organization. Lacking a discrete nucleus, these organisms are said to be prokaryotic.

Microorganisms of special concern to biochemical engineering include yeasts, bacteria, algae, and molds. The protozoa can feed on smaller organisms in natural waters and in waste-treatment processes but are not useful in producing materials of commercial value. Certain viruses called phages are also important in that they can infect microorganisms and may destroy a culture. A beneficial feature of microbial viruses is the ability to convey genetic materials from other sources into an organism. This is called transduction. Each species of microorganisms grows best within certain pH and temperature ranges, commonly between 20 and 40°C (68–104°F) and not too far from neutral pH.

Bacteria The bacteria are tiny single-cell organisms ranging from 0.5–20 μm in size, although some may be smaller, and a few exceed 100 μm in length. The cell wall imparts a characteristic round or ovoid, rod, or spiral shape to the cell. Some bacteria can vary in shape, depending on culture conditions; this is termed *pleomorphism.* Certain species are further characterized by the arrangement of cells in clusters, chains, or discrete packets. Some cells produce various pigments that impart a characteristic color to bacterial colonies. The cytoplasm of bacteria may also contain numerous granules of storage materials such as carbohydrates and lipids. Bacteria can contain plasmids that are pieces of genetic material existing outside the main genome. Plasmids can be used as vectors for introducing foreign genes into the bacteria that can impart new synthetic capabilities to an otherwise "wild" bacterial strain. Many bacteria exhibit motility by means of one or more hairlike appendages called flagella. Bacteria reproduce by dividing into equal parts, a process termed *binary fission.*

Under adverse conditions, certain microorganisms produce spores that germinate upon return to a favorable environment. Spores are a particularly stable form or state of bacteria that may survive dryness and temperature extremes. Some microorganisms form spores at a stage in their normal life cycle.

Many species may, under appropriate circumstances, become surrounded by gelatinous material that provides a means of attachment and some protection from other organisms. If many cells share the same gelatinous covering, it is called a slime; otherwise each is said to have a capsule.

Algae Algae are a very diverse group of photosynthetic organisms that range from microscopic size to giant kelp that may reach lengths of 20 m (66 ft). Some commercial biochemicals come from algal seaweeds, and algae supply oxygen and consume nutrients in some processes used for biological waste treatment. Although their rapid growth rates relative to other green plants offer great potential for producing biomass for energy or a chemical feedstock, there is little industrial use of algae. One proposed process uses Dunaliella, a species that grows in high salinity and accumulates glycerol internally to counter the high external osmotic pressure. Outdoor ponds are most suitable for growing algae because vast surfaces and high illumination are needed.

Fungi As a group, fungi are characterized by simple vegetative bodies from which reproductive structures are elaborated. All fungal cells possess distinct nuclei and produce spores in specialized fruiting bodies at some stage in their life cycles. The fungi contain no chlorophyll and therefore require sources of complex organic molecules for growth: Many species grow on dead organic material; others live as parasites.

Yeasts are one kind of fungi. They are unicellular organisms surrounded by a cell wall and possessing a distinct nucleus. With very few exceptions, yeasts reproduce by a process known as budding, where a small new cell is pinched off the parent cell. Under certain conditions, an individual yeast cell may become a fruiting body, producing spores.

Isolated Plant and Animal Cells Biotechnology includes recovery of biochemicals from intact animals and plants, but the care and feeding of them is beyond the scope of this section. Processes with their isolated cells have much in common with processes based on microorganisms. The cells tend to be much more fragile than microbial cells, and allowable ranges of pH and temperature are quite narrow. These cells occur in aggregates and usually require enzymes to free them. There is a strong tendency for the cells to attach to something, and cell cultures often exploit attachment to surfaces.

Plant and animal cells have numerous chromosomes. Growth rates are relatively slow. A typical nutrient medium will contain a large number of vitamins and growth factors in addition to complex nitrogen sources, because other specialized cells in the original structures supply these needs. A plant or animal cell is not like a microbial cell in its ability to function independently.

Viruses Viruses are particles of a size below the resolution of the light microscope and are composed mainly of nucleic acid, either DNA or RNA, surrounded by a protein sheath. Lacking metabolic machinery, viruses exist only as intracellular highly host-specific parasites. Many bacteria and certain molds are subject to invasion by virus particles. Those that attack bacteria are called bacteriophages. They may be either virulent or temperate (lysogenic). Virulent bacteriophages divert the cellular resources to the manufacture of phage particles; new phage particles are released to the medium as the host cell dies and lyses. Temperate bacteriophages have no immediate effect upon the host cell; they become attached to the bacterial chromosome. They may be carried through many generations before being triggered to virulence by some physical or chemical event.

Biochemistry All organisms require sources of carbon, oxygen, nitrogen, sulfur, phosphorus, water, and trace elements. Some have specific vitamin requirements as well. Green plants need only carbon dioxide, nitrate or ammonium ions, dissolved minerals, and water to manufacture all of their cellular components. Photosynthetic bacteria require specific sources of hydrogen ions, and the chemosynthetic bacteria must have an oxidizable substrate. Some microorganisms have the ability to "fix" atmospheric nitrogen by reduction. Organisms that use only simple inorganic compounds as nutrients are said to be *autotrophic* (self-nourishing).

Organisms that require compounds manufactured by other organisms are called *heterotrophs* (other-nourishing). Many heterotrophs secrete enzymes (exoenzymes) that hydrolyze large molecules such as starch and cellulose to smaller units that can readily enter the cell.

Proteins are macromolecules that play many roles such as serving as enzymes or components of cell membranes and muscle. The antibodies that protect against invasion by foreign substances are themselves proteins. There are twenty-odd amino acids found regularly in most naturally occurring proteins. Because of the great length of protein chains and the various sequences of amino acids, the theoretical number of possible proteins is astronomical. The amino acid sequence is referred to as the primary structure of a protein. The polypeptide

chain is usually coiled or folded to provide secondary structure to the molecule, and linkages through other functional groups (mainly disulfide bonds) form the tertiary structure. For some protein molecules, there may be spatial arrangement forming defined aggregates, known as the quarternary structure of proteins. For a polypeptide polymer to have biological activity a certain molecular arrangement is necessary. This requires not only the primary and secondary but also tertiary and sometimes quarternary structure. Such a strict structural requirement explains the high specificity of proteins. In the presence of certain chemical reagents, excessive heat, radiation, unfavorable pH, and so on, the protein structure may become disorganized. This is called *denaturation* and may be reversible if not too severe.

A special class of proteins, the enzymes, are biological catalysts that expedite reactions by lowering the amount of activation energy required for the reactions to go. An enzyme has an active site that may be thought of as an atomic vise that orients a portion of a molecule for its reaction. The rest of the enzyme is not just an inert glob. Regions that are recognized by antibodies enable living systems to identify and inactivate foreign proteins. Immunological reactions involving antibodies are a defense against such foreign proteins. Enzymes function in conjunction with another special class of compounds known as coenzymes. Coenzymes are not proteins; many of the known coenzymes include vitamins, such as niacin and riboflavin, as part of their molecular structure. Coenzymes carry reactant groups or electrons between substrate molecules in the course of a reaction. As coenzymes serve merely as carriers and are constantly recycled, only small amounts are needed to produce large amounts of biochemical product.

Hundreds of metabolic reactions take place simultaneously in cells. There are branched and parallel pathways, and a single biochemical may participate in several distinct reactions. Through mass action, concentration changes caused by one reaction may effect the kinetics and equilibrium concentrations of another. In order to prevent accumulation of too much of a biochemical, the product or an intermediate in the pathway may slow the production of an enzyme or may inhibit the activation of enzymes regulating the pathway. This is termed feedback control and is shown in Fig. 24-1. More complicated examples are known where two biochemicals act in concert to inhibit an enzyme. As accumulation of excessive amounts of a certain biochemical may be the key to economic success, creating mutant cultures with defective metabolic controls has great value to the production of a given product.

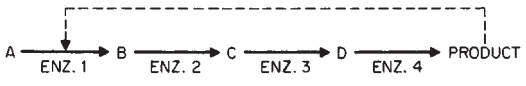


FIG. 24-1 Feedback control. Product inhibits the first enzyme.

Cell efficiency is improved by inhibiting or regulating the synthesis of unneeded enzymes, so there are two classes of enzymes—those that are constitutive and always produced and those that are inducible, i.e., synthesized when needed in response to an inducer, usually the initial substrate in a pathway. Enzymes that are induced in one organism may be constitutive in another.

Microorganisms exhibit nutritional preferences. The enzymes for common substrates such as glucose are usually constitutive, as are the enzymes for common or essential metabolic pathways. Furthermore, the synthesis of enzymes for attack on less common substrates such as lactose is repressed by the presence of appreciable amounts of common substrates or metabolites. This is logical for cells to conserve their resources for enzyme synthesis as long as their usual substrates are readily available. If presented with mixed substrates, those that are in the main metabolic pathways are consumed first, while the other substrates are consumed later after the common substrates are depleted. This results in diauxic behavior. A diauxic growth curve exhibits an intermediate growth plateau while the enzymes needed for the uncommon substrates are synthesized (see Fig. 24-2). There may also be preferences for the less common substrates such that a mixture shows a sequence of each being exhausted before the start of metabolism of the next.

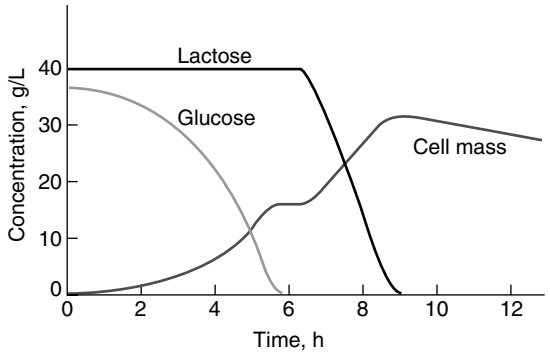


FIG. 24-2 Computer simulation of typical diauxic behavior.

Energy Many metabolic reactions, once activated, proceed spontaneously with a net release of energy. Hydrolysis and molecular rearrangements are examples of spontaneous reactions. The hydrolytic splitting of starch to glucose, for instance, results in a net release of energy. But a great many biochemical reactions are not spontaneous and therefore require an energy input. In living systems this requirement is met by coupling an energy-requiring reaction with an energy-releasing reaction. If a sufficient amount of energy is produced by a metabolic reaction, it may be used to synthesize a high-energy compound such as adenosine triphosphate (ATP). When the terminal phosphate linkage is broken, adenosine diphosphate (ADP) and inorganic phosphate are formed, and energy is provided. When sufficient energy becomes available, ATP is reformed from ADP.

In biological systems, the most frequent mechanism of oxidation is the removal of hydrogen, and conversely, the addition of hydrogen is the common method of reduction. Nicotinamide-adenine dinucleotide (NAD) and nicotinamide-adenine dinucleotide phosphate (NADP) are two coenzymes that assist in oxidation and reduction. These cofactors can shuttle between biochemical reactions so that one drives another, or their oxidation can be coupled to the formation of ATP. However, stepwise release or consumption of energy requires driving forces and losses at each step such that overall efficiency suffers.

Overall redox potential of a system determines the amount of energy that cells can derive from their nutrients. When oxygen is present to be the ultimate acceptor of electrons, complete oxidation of organic molecules yields maximum energy and usually results in the production of H_2O and CO_2. However, inside animals, in polluted waters, in the benthos (bottom region) of natural waters, and elsewhere, there is little or no free oxygen. In these environments, organisms develop that can partially oxidize substrates or can derive a small amount of energy from reactions where some products are oxidized while others are reduced. The pathways for complete oxidation may be absent and the presence of oxygen can disrupt the mechanisms for anaerobic metabolism so that the cell is quickly killed. The differences in efficiency are striking: Aerobic metabolism of one molecule of glucose can generate bond energy as much as 33 molecules of ATP, while anaerobic metabolism can yield as little as two molecules of ATP. Natural anaerobic processes accumulate compounds such as ethanol, acetoin, acetone, butanol, lactate, and malate. Products of natural aerobic metabolism are water and carbon dioxide, cell mass, and secondary metabolic products such as antibiotics.

Photosynthesis All living cells synthesize ATP, but only green plants and a few photosynthetic (or phototrophic) microorganisms can drive biochemical reactions to form ATP with radiant energy through the process of photosynthesis. All photosynthetic organisms contain one or more of the group of green pigments called chlorophylls. In plants, these are contained in organelles called chloroplasts. The number per cell of membrane-surrounded chloroplasts varies with species and environmental conditions. In higher plants, numerous chloroplasts are found in each cell of the mesophyll tissue of leaves, while an algal cell may contain a single chloroplast. A chloroplast has a sand-

wich of many layers alternating between pigments and enzymatic proteins such that electromagnetic excitation from light becomes chemical bond energy. Prokaryotic organisms have a unique type of chlorophyll and do not possess chloroplasts organelles. Instead, their photosynthetic systems are associated with the cell membrane or with lamellar structures located in organelles known as chromatophores. Chromatophores, unlike chloroplasts, are not surrounded by a membrane.

The net result of photosynthesis is reduction of carbon dioxide to form carbohydrates. A key intermediate is phosphoglyceric acid, from which various simple sugars are produced and disproportionated to form other carbohydrates.

Mutation and Genetic Engineering Exposing organisms to agents such as mustard chemicals, ultraviolet light, and x-rays increases mutation rate by damaging chromosomes. In strain development through mutagenesis, the idea is to limit the mutagen exposure to kill about 99 percent of the organisms. The few survivors of this intense treatment are usually mutants. Most of the mutations are harmful to the cell, but a very small number may have economic importance in that impaired cellular control may result in better yields of product. The key is to have a procedure for selecting out the useful mutants. Screening of many strains to find the very few worthy of further study is tedious and expensive. Such screening that was so very important to biotechnology a few decades ago is becoming obsolete because of genetic improvements based on recombinant DNA technology.

Whereas mutagenic agents delete or scramble genes, recombinant DNA techniques add desirable genetic material from very different cells. The genes may come from plant, animal, or microbial cells, or in a few instances they may be synthesized in the laboratory from known nucleic acid sequences in natural genes. Opening a chromosome and splicing in foreign DNA is simple in concept, but there are complications. Genes in fragments of DNA must have control signals from other nucleic acid sequences in order to function. Both the gene and its controls must be spliced into the chromosomes of the receiving culture. Bacterial chromosomes (circular DNA molecules) are cut open with enzymes, mixed with the new fragments to be incorporated, and closed enzymatically. The organism will acquire new traits. This technique is referred to as recombinant technology.

There are many tricks and some art in genetic engineering. Examples would be using bacteriophage infection to introduce a gene for producing a new enzyme in a cell. Certain strains of *E. coli, B. subtilis,* yeast, and streptomyces are the usual working organisms (cloning vectors) to which genes are added. The reason for this is that the genetics of these organisms is well understood and the methodology has become fairly routine.

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CELL AND TISSUE CULTURES

Mammalian Cells Unlike microbial cells, mammalian cells do not continue to reproduce forever. Cancerous cells have lost this natural timing that leads to death after a few dozen generations and continue to multiply indefinitely. Hybridoma cells from the fusion of two mammalian lymphoid cells, one cancerous and the other normal, are important for mammalian cell culture. They produce monoclonal antibodies for research, for affinity methods for biological separations, and for analyses used in the diagnosis and treatment of some diseases. However, the frequency of fusion is low. If the unfused cells are not killed, the myelomas will overgrow the hybrid cells. The myelomas can be isolated when there is a defect in their production of enzymes involved in nucleotide synthesis. Mammalian cells can produce the necessary enzymes and thus so can the fused cells. When the cells are placed in a medium in which the enzymes are necessary for survival, the myelomas will not survive. The unfused normal cells will die because of their limited life span. Thus, after a period of time, the hybridomas will be the only cells left alive.

A hybridoma can live indefinitely in a growth medium that includes salts, glucose, glutamine, certain amino acids, and bovine serum that provides essential components that have not been identified. Serum is expensive, and its cost largely determines the economic feasibility of a particular culture system. Only recently have substitutes or partial replacements for serum been found. Antibiotics are often included to prevent infection of the culture. The pH, temperature and dissolved oxygen, and carbon dioxide concentration must be closely controlled. The salt determines the osmotic pressure to preserve the integrity of the fragile cell.

Most glucose is metabolized to lactate because glycolysis is usually much faster than uptake rate of glycolytic intermediates. Glutamine acts as the primary source of nitrogen as well as providing additional carbon and energy. After glutamine is partially oxidized to glutamate, it can enter the TCA cycle and emerge as pyruvate. It has been estimated that between 30 and 65 percent of the cell energy requirement is derived from glutamine metabolism when both glucose and glutamine are available. Ammonia is produced in the deamination of glutamine to form glutamate and in the formation of alpha-ketoglutarate.

Plant Cells and Tissues It is estimated that today some 75 percent of all pharmaceuticals originate in plants. Typically, these compounds are derived from the secondary metabolic pathways of the cells. When plant or animal cells are cultured, concepts from microbiology come into play. Only specialized cells are used, and these can be improved with mutation, selection, and recombinant DNA techniques. One very major difference between cell and tissue cultures and most microbiological processes is very high susceptibility to contamination by foreign organisms. Most microorganisms grow rapidly and compete well; some are aided by their own changes to the environment. When a microbial process changes the pH to be far from neutrality or when the product such as ethanol is inhibitory to other organisms, growth of contaminants is discouraged. Cell and tissue cultures require rich media and are characterized by slow growth rates. There is seldom any protection by the products of the process. Optimum conditions for production of the secondary metabolites are not likely to be the same as for growth. Economics may hinge on a good balance of growing sufficient cells and favoring product formation.

Only a few biochemicals derived from plant cell and tissue cultures have high volume/low value products, but some have sizeable markets as specialty chemicals such as dyes, fragrances, insecticides, and pesticides. These differ from the low volume/very high value compounds that typify life-saving drugs and pharmaceuticals. Examples for both of these categories are listed in Table 24-1 along with the plant species of origin.

Because of cell specialization, some products are produced in cultures of those cellular types. Three main classifications of the types of plant cell and tissue cultures are:

Undifferentiated cell cultures. Aggregate clumps of cells on solid media (callus) or in liquid media (suspension)

Protoplast cultures. Cellular tissues devoid of cell wall material in culture

Organ cultures. Differentiated tissues of shoots, roots, anthers, ovaries, or other plant organs in culture

Primary Growth Requirements Primary growth is defined as the processes in a plant that are essential for the growth of the meristematic regions such as the shoot apex, root tip, and axillary meristems. Plant cell and tissue cultures have specific optima for their primary growth in terms of lighting, temperature, aeration, a nutrient medium that must supply a carbon source, vitamins, hormones, and inorganic constituents and with pH typically between 5.5 and 6.5. Aeration can be critical depending upon the species.

TABLE 24-1 Typical Products Derived from Plants

Compound	Application	Volume/ value	Source
Shikonin	Dye	High/low	*Lithospermum erthrorhizon*
Warfarin	Pesticide	High/low	Sweet clover
Gossypol	Pesticide/anti-fertility	Low/high	Cotton
Scopolamine	Antispasmodic	Low/high	*Daturastramonium*
Ajmalicine	Circulatory agent	Low/high	*Catharanthusroseus*
Taxol	Anticancer	Low/high	California yew tree

Although a few exceptions do exist where glucose, fructose, or galactose is preferred, the majority of the plant cultures use sucrose. Usual trace requirements are thiamine, niacin, riboflavin, pyridoxine, choline, ascorbic acid, and inositol. Hormones such as auxins and cytokinins promote an undifferentiated state or trigger differentiation into specific plant tissues. As with the whole plant, cellular groups, either differentiated or undifferentiated, require a set of inorganic elements such as nitrogen, phosphorus, potassium, magnesium, calcium, sulfur, iron, chlorine, boron, manganese, and zinc. The exact compositions and concentrations of these inorganic elements that are optimum for a particular plant species can be highly variable. However, prepackaged formulations of these salts that can even include the carbon source, vitamins, hormones, and pH buffers are commercially available.

Secondary Metabolic Requirements A difference between the growth and secondary metabolic phase is that the latter gains importance when approaching the reproductive stages. For example, many of the pigments of flowers are secondary metabolites (e.g., shikonin). Secondary mechanisms are typical responses to stress, such as change in pH (e.g., alkaloid production in *Hyocyamus muticus* cell cultures is optimum at pH 3.5, while growth is best at 5.0). Similarly, carbon-source concentrations affect *Morinda citrifolia* cell cultures that grow best at 5 percent sucrose but produce the anthraquinone secondary metabolites optimally at 7 percent. Temperature changes can cause flowering; several plants require a cold treatment to induce flowering. This is called *vernalization.* Secondary metabolic pathways in plant cell and tissue cultures seem to be highly controlled by the hormone level in the medium. Another method of eliciting secondary metabolites employs the natural defense mechanisms of the plants that have developed through evolution. For example, gossypol produced by *Gossypium hirsutum* (cotton) cells is a natural response of the plant when subjected to the infections of the wilt-producing fungus *Verticillium dahliae.*

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RECENT EMPHASES

Commercial use of cell and tissue culture continues to expand. Improvement of organisms through recombinant nucleic acid techniques has become commonplace. Formerly, a few laboratories were well ahead of most others, but now the methods have been perfected for routine use. Another technique that is widely practiced is culturing of cells that excrete high concentrations of just one antibody protein. The specificity of antibodies and antigens is exploited in medical testing procedures using these pure monoclonal antibodies.

Environmental issues are driving several aspects of biotechnology. Sites contaminated by toxic wastes can be cleaned by several alternative methods, but all are expensive. The most certain way to remove toxic materials from soil is to excavate it for incineration, but this requires much labor, energy, and money. Bioremediation in situ tends to be much less expensive on one hand but is slow and uncertain on the other. Microbial growth rates approach zero as nutrient levels fall to the low concentrations required for approval of the toxic site remediation. This means that rates tend to be unacceptable when striving for complete removal. Many toxic materials do not support growth of microorganisms. However, they may be degraded as the microorganisms grow on other nutrients. This is termed *cometabolism.*

Materials that are easily biodegraded could substitute for plastics and other organic chemicals that damage the environment. There has been some progress with natural surfactants produced by microorganisms; these would be used in detergents if properties were acceptable and costs were competitive. Biodegradable polymers such as poly-beta-hydroxybutyrate or its derivatives should eventually substitute for polyethylene and polypropylene, but costs are still too high.

BIOLOGICAL REACTORS

FERMENTERS

The term *fermentation* formerly distinguished processes from which air was absent, but the term has now been extended to aerobic processes. Bioprocessing is usually aseptic (free of unwanted organisms) in vessels held under positive pressure of sterile air to resist entry of contaminating microorganisms. A few processes such as the production of pathogenic organisms for medical purposes or for biological warfare operate below atmospheric pressure because safety of the plant operators is more important than the integrity of the product. Older processes such as manufacture of pickles had no special measures against contamination, but many of these have been converted to aseptic operations to prevent impairment of product quality by foreign organisms. Biological waste treatment employs elective cultures of microorganisms in relatively crude, open equipment.

Activities associated with bioreactors include gas/liquid contacting, on-line sensing of concentrations, mixing, heat transfer, foam control, and feed of nutrients or reagents such as those for pH control. The workhorse of the fermentation industry is the conventional batch fermenter shown in Fig. 24-3. Not shown are ladder rungs inside the vessel, antifoam probe, antifoam system, and sensors (pH, dissolved oxygen, temperature, and the like). Note that coils may lie between baffles and the tank wall or connect to the top to minimize openings below the water level, and bottom-entering mixers are used frequently. There is extensive process piping, and copper or brass fittings are taboo for some processes because of highly deleterious effects of copper (more than 50 percent reduction in yield has been noted in penicillin fermentations when a bronze valve was in a feed line). Cooling coils must be used for larger tanks because the heat-transfer area of a jacket is inadequate for cooling from sterilization temperature to operating temperature in a reasonable time. Some features of interest for a conventional fermenter are that (1) a bypass valve in the air system allows diversion of air so that foaming is not excessive and the redox potential is not too high during the early stage of fermentation when the inoculum is becoming established; (2) antifoam is added when excessive foam reaches a conductive or capacitive electronic probe; (3) all piping is sterilized by the use of steam and is protected by steam until put into use; (4) the level of liquid when filling the vessel is determined by reference to a calibration chart based on points in the tank such as a rung on the ladder; (5) the weight of the tank contents can be determined by the hydrostatic balance against air bubbled slowly through the sparger; and (6) pumps are very uncommon because it is so easy to force fluid from a pressurized vessel.

The need for highly cost-efficient oxygen transfer in fermentations such as those with hydrocarbon feedstocks has led to air-lift fermenters as shown in Fig. 24-4. The world's largest industrial fermenter was

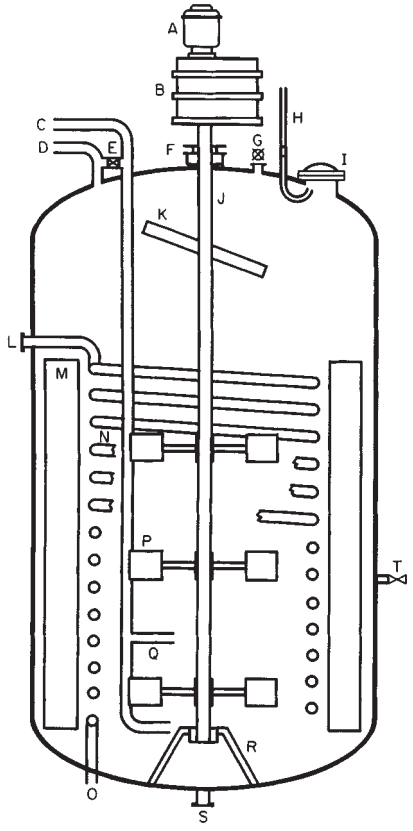


FIG. 24-3 Conventional batch fermenter. *A* = agitator motor; *B* = speed-reduction unit; *C* = air inlet; *D* = air outlet; *E* = air bypass valve; *F* = shaft seal; *G* = sight glass with light; *H* = sight-glass clean-off line; *I* = manhole with sight glass; *J* = agitator shaft; *K* = paddle to break foam; *L* = cooling-water outlet; *M* = baffle; *N* = cooling coils; *O* = cooling-water inlet; *P* = mixer; *Q* = sparger; *R* = shaft bearing and bracket; *S* = outlet (steam seal not shown); *T* = sample valve (steam seal not shown).

designed for producing single-cell protein from hydrocarbons at Billingham, England, U.K. Its dimensions are 100 m (328 ft) in height and 10 m (33 ft) in diameter.

A few variations on the standard fermenter have been attempted, but none has become popular. An obsolete design in which the fermenter was rotated to aerate the medium is shown in Fig. 24-5. Performance was unsatisfactory, and the units were turned on end, with spargers and agitation added. One of the largest fermenters used for antibiotics is a horizontal cylinder with several agitators, as in Fig. 24-6. Multiple agitator motors and shafts have also been used with vertical cylindrical vessels.

Another innovative design is the toroidal fermenter shown in Fig. 24-7. Motion in an axial direction allows intimate mixing with air. A special case of the air-lift fermenter is shown in Fig. 24-8. The feed enters at moderate pressure and is drawn downward to regions of very high hydrostatic pressure that provides a great driving force for gas transfer. In the other leg, lowering pressure allows gases to expand to induce circulation. Experimental units have been built in elevator shafts.

Ethanol fermentation is a particularly good example of product accumulation inhibiting the microbial culture. Most strains of yeast have a much slower alcohol production rate when ethanol reaches about ten percent, and the wine or saki strains that achieve over 20 percent by volume of ethanol are very, very slow. A system known as the Vacuferm for removal of alcohol by distillation as it is formed is

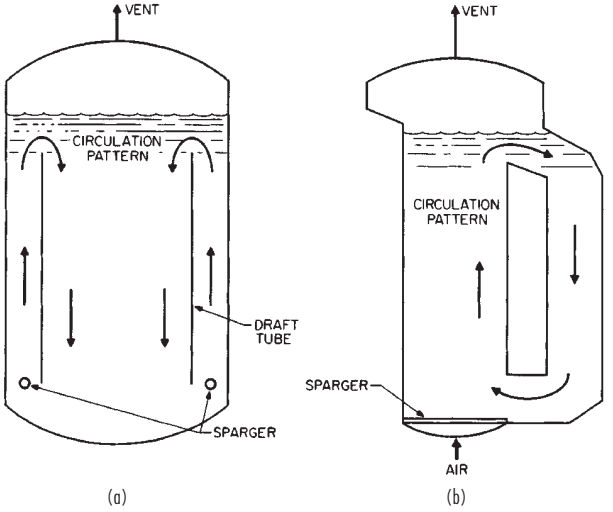


FIG. 24-4 Air-lift fermenters: (*a*) Concentric cylinder; (*b*) external recycle.

shown in Fig. 24-9. The vacuum is adjusted to the vapor pressure of the alcohol-water solution at the fermentation temperature, 30 to 40°C (86 to 104°F). Volumetric productivity is far better than that of a conventional fermenter, but there is a killing disadvantage of having to recompress large volumes of vapor so that alcohol can be condensed with normal cooling water instead of expensive cold brine. Furthermore, the large amounts of carbon dioxide generated by fermentation are evacuated and recompressed along with the alcohol and water vapors. A far better design is shown in Fig. 24-10, where the fermenter operates at normal pressure so that carbon dioxide escapes, and broth is circulated through the flash pot for vaporization of the ethanol. Although this system may seem to have attractive energy economy because metabolic heat is removed as the vapor flashes,

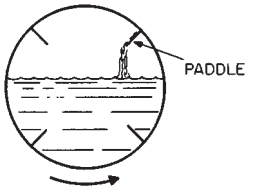


FIG. 24-5 Rotating fermenter.

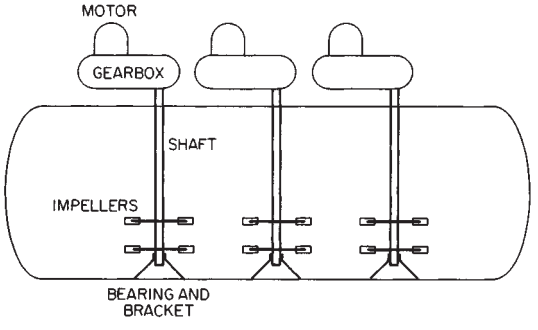


FIG. 24-6 Horizontal fermenter.

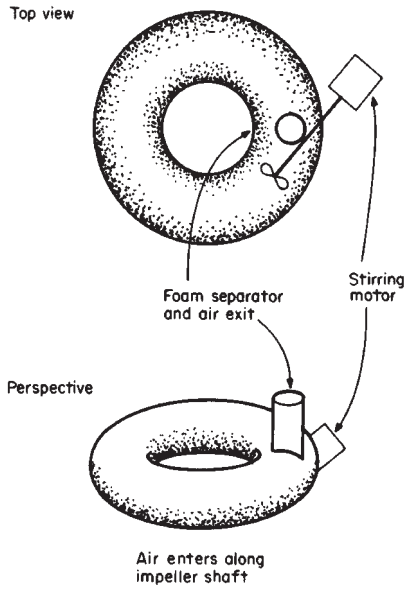


FIG. 24-7 Toroidal fermenter.

initial investment and the cost of pumping the vapors are high. Operating the ethanol fermentation at higher temperatures with thermophillic organisms has better economics in terms of milder vacuum and less recompression because of the higher vapor pressure, but evolving carbon dioxide can strip out product. Other alternatives for overcoming inhibition by the product are extraction from the fermentation broth with an immiscible solvent and/or operating with very dense cultures so that low productivity per cell is compensated by having many more cells.

Elevated cell concentrations can be achieved by separating cells from the effluent and recycling them to the fermenter. This has been

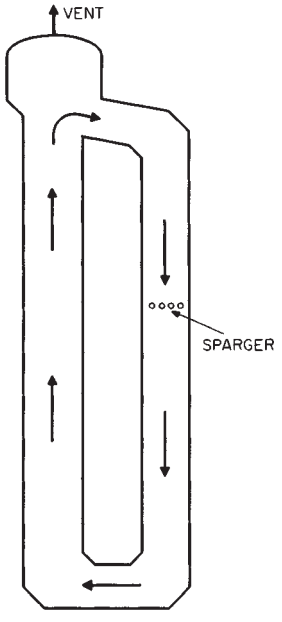


FIG. 24-8 Deep-shaft fermenter.

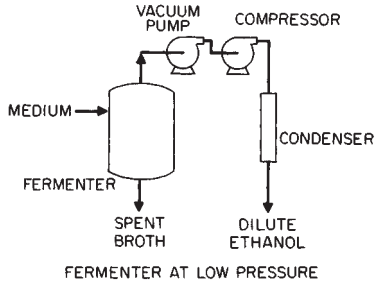


FIG. 24-9 Vacuferm.

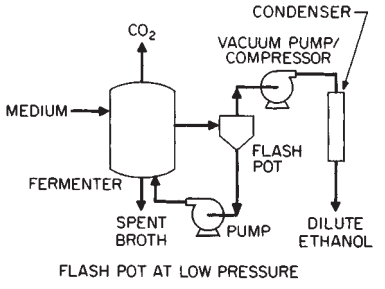


FIG. 24-10 Flash-pot fermenter.

standard practice for many years in biological waste treatment where dilute feed streams result in slow growth of the culture. Producing cell flocs that are collected easily by sedimentation is aided by recycling those cells that do settle. This is a selective advantage that may allow them to dominate. Industrial fermentations can afford more expense than can waste treatment, and centrifuges for collecting cells are not uncommon. Recycle of yeast cells can lower the fermentation time for ethanol significantly. Heavily coagulated cells can be retained in the fermenter; the tower fermenter shown in Fig. 24-11 uses this principle with yeast strains that flocculate naturally. Cells can also be retained in the reactor by attachment to a support. Vinegar is sometimes produced in a generator filled with wood shavings to which bacteria attach. Rocks or plastic support materials are used in trickling filters for waste treatment (see Sec. 25). Chemical agents can link cells to the support materials when simple adsorption does not hold them tightly enough. Gel entrapment can provide extremely high cell concentrations because the cells continue to multiply within the gel. Comparisons of results with fermentation of ethanol are in Table 24-2.

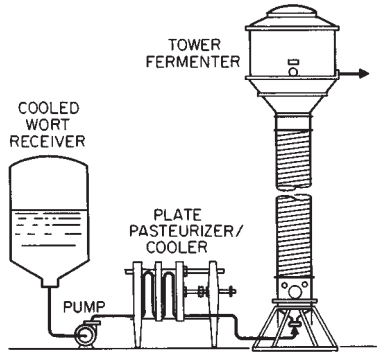


FIG. 24-11 Tower fermenter. (*Compliments of APV Corp.*)

TABLE 24-2 Comparison of Ethanol Fermenters

System	Typical time (h)	Typical ethanol concentration (%)
Conventional	72	10
Cell recycle	12	8
Tower fermenter	3	8
Gel immobilization	1	10

PROCESS CONSIDERATIONS

Fermentation can be combined with other operations. For example, feedback inhibition of enzymatic hydrolysis of cellulose can be relieved by removal of the product glucose by fermentation as it forms. This is termed *simultaneous-saccharification-fermentation* (SSF).

Valves and pumps that have a potential path for contaminating organisms are taboo for aseptic operations. Rising stem valves could bring organisms to the sterile side by the in and out motion as the valve operates. Diaphragm valves are still commonly used, but heating, cooling, and the abrasion by solids in the nutrient media are somewhat severe conditions leading to occasional rupture of a diaphragm and contamination of a run. Ball valves or plug valves do not have an absolute seal to the outside, but the direction of motion does not tend to bring organisms in. Contamination is seldom attributed to these valves; they are designed for easy maintenance in place, and there is the very nice human advantage that a glance at the handle tells easily whether the valve is open or closed. Many runs have been spoiled or impaired because a manual valve was left in the wrong position. For plant operations, pumps with diaphragms are satisfactory. In the lab or pilot plant, peristaltic pumps (also known as tubing squeezers) predominate.

Transfer of fluid in a fermentation plant usually makes use of air pressure differences. One or more manifold headers may interconnect many vessels. As transfers may have to be aseptic, headers are pressurized with steam until needed. A typical arrangement of steam seals is shown in Fig. 24-12.

Sample lines commonly have steam seals too. A typical layout is shown in Fig. 24-13. In the closed position, steam provides an absolute barrier to contamination. To take a sample, the steam line and the trap line are closed, and fermentation medium is flowed to waste until the pipes are cool to the touch so that sensitive products do not give false assays because of thermal destruction. Cooling takes up to 5 liters of medium if not done carefully, and bad practices can waste considerably more. Pilot-sized tanks have less massive fittings that are easier to cool; less medium is wasted, but oversampling to the point where the fermenter volume is low can be a problem. For this reason, alternate sampling methods have been devised. For example, a sterile syringe and needle may be used to sample through a rubber diaphragm in the wall of the tank. Although such methods appear reliable, there is a tendency to scrap all innovations and to return to tried and true steam seals when the factory encounters any period of contamination.

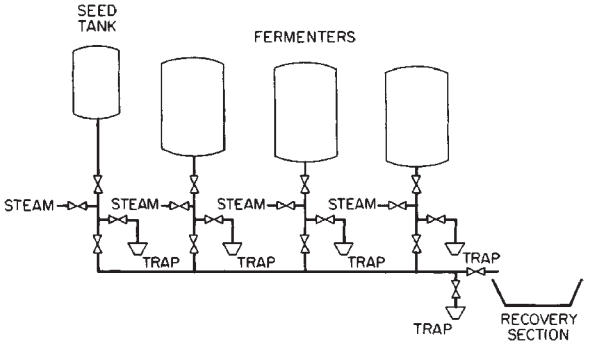


FIG. 24-12 Inoculation and harvest header.

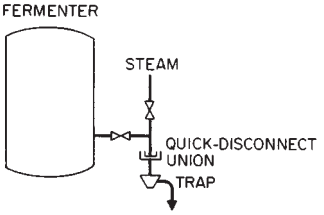


FIG. 24-13 Sample-line piping. (A valve to the sewer allows bypass of the trap while cooling the line.)

All piping to a fermenter is flushed with steam during the sterilization period. A clever means for sight-glass cleaning uses steam condensate that is naturally sterile in a dead leg. Steam pressure behind the condensate forces this water to the sight glass. Without cleaning, splashing and spray can quickly cover the sight glass with a thick coating of microorganisms and medium.

While it is easy to add materials to a fermentation, removal is difficult. Membrane devices have been placed in the fermenter or in external recycle loops to dialyze away a soluble component. Cells release wastes or metabolites that can be inhibitory; these are sometimes referred to as *staling factors.* Their removal by dialysis has allowed cell concentrations to reach ten to one hundred times that of control cultures.

Solid substrates such as pulverized wood cannot be stirred when slurry concentration exceeds about 5 percent. For saccharification prior to ethanol fermentation, keeping sugar concentration high can avoid an evaporation step. In a batch reactor, mixing limitations with the wood results in a dilute sugar solution. This has been circumvented by placing the wood in a column and percolating the solution through. As wood dissolves, more is added. Simultaneous fermentation of the sugars formed in the column is possible.

Oxygen Transfer Supplying sufficient oxygen can be a very challenging engineering problem for some aerobic fermentations. Oxygen is sparingly soluble in water; saturation with pressurized air at room temperature provides only 6 or 7 milligrams per liter of oxygen. A vigorous process can deplete the dissolved oxygen in several seconds when aeration is stopped. Mass transfer of gases to liquids is covered in Sec. 5. Emphasis is somewhat different for biological systems that commonly have bubble aeration. Because the number and size of bubbles is very difficult to estimate, transfer area is usually lumped with the mass-transfer coefficient as a $K_l a$ term. The "l" subscript in K_l signifies that liquid film resistance should greatly predominate for a sparingly soluble gas such as oxygen. The relationship between oxygen concentration and growth is of a Michaelis-Menten type (see Fig. 24-20). When a process is rate-limited by oxygen, the specific respiration rate (Q_{O2}) also increases steeply with dissolved oxygen concentration until a plateau is reached. The concentration below which respiration is severely limited is termed the critical oxygen concentration, which typically ranges from 0.5 to 2.0 ppm for well-dispersed bacteria, yeast, and fungi growing at 20 to 30°C (68 to 86°F). Above this critical concentration, the specific oxygen uptake increases only slightly with increasing oxygen concentrations.

A plot of the specific respiration rate Q_{O2} versus the specific growth rate coefficient μ is linear, with the intercept on the ordinate equal to the oxygen uptake rate for cell maintenance. A formulation of this is:

$$\text{Uptake rate} = \text{uptake for maintenance} + \text{uptake for growth}$$

or

$$Q_{O2}X = \frac{(Q_{O2})_M X + \mu X}{Y_g} \qquad (24\text{-}1)$$

where X is organism concentration, the subscript M denotes maintenance, Y_g is yield of cell mass per mass of oxygen, and the Q terms signify oxygen uptake rates in mass O_2 per mass of organisms.

This type of correlation applies to almost any substrate involved in cellular energy metabolism and is supported by experimental data and energetic considerations. However, it is based on assumptions true at or near the steady-state equilibrium conditions and may not be valid

during transient states. The oxygen-uptake equation should be modified when other cellular activities requiring oxygen can be identified. For example, use of oxygen for product formation would be represented by:

Uptake rate = maintenance uptake + growth uptake + product uptake

or
$$Q_{O2}X = (Q_{O2})_M X + \frac{dX}{dt}\frac{1}{Y_G} + \frac{dP}{dt}\frac{1}{Y_P} \qquad (24\text{-}2)$$

where P is the product concentration and Y is the yield of product per unit weight of limiting nutrient. Oxygen uptake is distributed between that for growth and that for cellular activities dependent on cell concentration.

As the oxygen transfer rate under steady-state conditions must equal oxygen uptake, K_la may be calculated:

$$K_la = \frac{\text{overall oxygen uptake rate}}{(C^* - C)_{\text{mean}}} \qquad (24\text{-}3)$$

where C^* = concentration of oxygen in the liquid that would be in equilibrium with the gas-bubble concentration and K_la = the volumetric oxygen transfer rate.

A convenient method for measuring oxygen transfer rates in microbial systems depends on dissolved oxygen electrodes with relatively fast response times. Quite inexpensive oxygen electrodes are available for use with open systems, and steam-sterilizable electrodes are available for aseptic systems. There are two basic types: One develops a voltage from an electrochemical cell based on oxygen, and the other is a polarographic cell whose current depends on the rate at which oxygen arrives. See Fig. 24-14. Measurement of oxygen transfer properties requires only a brief interruption of oxygen supply. A mass balance for oxygen is:

$$\frac{dO}{dt} = \text{rate of supply} - \text{uptake rate} \qquad (24\text{-}4)$$

A tracing of the electrode signal during a cycle of turning aeration off and on is shown in Fig. 24-15. The rate of supply is zero (after bubbles have escaped) in the first portion of the response curve; thus, the slope equals the uptake rate by the organisms. When aeration is resumed, both the supply rate and uptake rate terms apply. The values for $C^* - C$ can be calculated from the data, the slope of the response curve at a given point is measured to get dC/dt, and the equation can be solved for K_la because all the other values are known.

Measurements of the rate of change in concentration of oxidizable chemicals in aerated vessels have questionable value for assessing rates with biological systems. Not only are flow patterns and bubble sizes different for biological systems, but surface active agents and

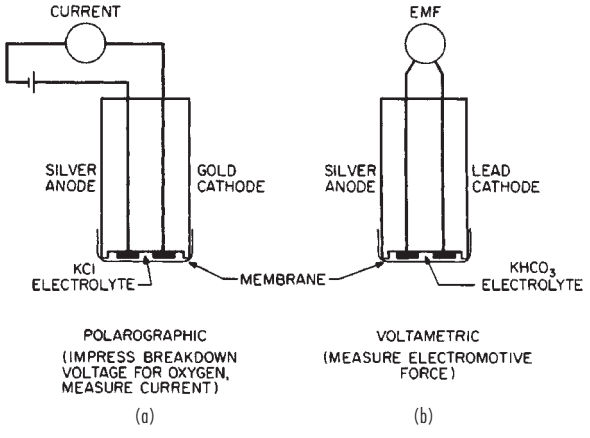


FIG. 24-14 Dissolved-oxygen electrodes: (*a*) polarographic (impress breakdown voltage for oxygen; measure current); (*b*) voltametric (measure electromotive force).

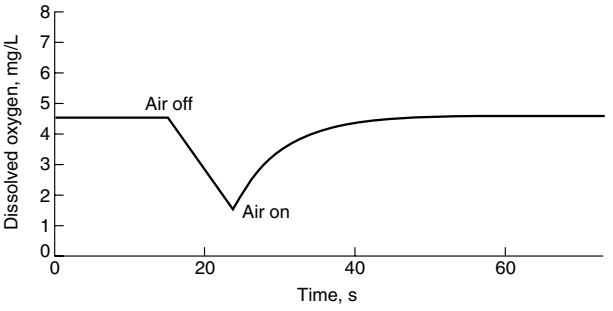


FIG. 24-15 Computer simulation of response for dynamic measurement of K_la.

suspended particles can seriously impair gas transfer. Fig. 24-16 shows the effects of various particles. In general, spherical particles have a small effect, elongated particles have more effect, and entangled particles markedly impair transfer. As many mold cultures are intertwined and lipids and proteins are present with strong surface activity, oxygen transfer to a fermentation can be much slower than that to simple aqueous solutions.

Except as an index of respiration, carbon dioxide is seldom considered in fermentations but plays important roles. Its participation in carbonate equilibria affects pH; removal of carbon dioxide by photosynthesis can force the pH above 10 in dense, well-illuminated algal cultures. Several biochemical reactions involve carbon dioxide, so their kinetics and equilibrium concentrations are dependent on gas concentrations, and metabolic rates of associated reactions may also change. Attempts to increase oxygen transfer rates by elevating pressure to get more driving force sometimes encounter poor process performance that might be attributed to excessive dissolved carbon dioxide.

Sparger Systems Gas distributors in tanks are shown in Sec. 6. Large openings are desirable for spargers in industrial fermentations to avoid clogging by microbial growth, but the diameter is usually designed for the acoustic velocity that insures small bubbles. Relatively small holes or diffusers are used in activated sludge units for biological waste treatment, but there is commonly a means for swinging a section of the aerator out of the vessel for cleaning. Newer designs for fermenters were conceived as answers to the problems of oxygen transfer. The air lift fermenter (Fig. 24-4) creates intimate mixing of air and medium while using the buoyancy of the gas to mix the fluid.

Surface active substances also lead to foaming that can be so bad that most of the contents of the fermenter are lost. Mechanical antifoam devices are helpful but cannot function alone except when there is little propensity for foaming. The mechanical foam breakers rupture the large, weak bubbles while allowing tiny, rugged bubbles to accumulate. Surface active antifoam agents tend to reduce elasticity of the bubbles so that mechanical shocks are easily transmitted to encourage rupture. Several antifoam delivery systems are shown in Fig. 24-17. Some lipids used as antifoams are metabolized by the culture and must be replaced. The nutrition supplied by these oils may be beneficial, but they are much more expensive than their equivalents in carbohydrate nutrients. Furthermore, it is troublesome to have nutrition coupled to foam control. Several synthetic antifoam agents are not nutrients and tend to persist. Their tendency to be lost by coating solid surfaces in the fermenter means that more must be added occasionally. These synthetic antifoam agents are toxic to some organisms, but one of the many types is usually satisfactory.

Scale-Up Fermenters ranging from about two to over 100 liters (0.07–3.5 ft^3) have been used for research and development, but the smaller sizes provide too little volume for sampling and are difficult to replicate, while large vessels are expensive and use too much medium. Autoclavable small fermenters that are placed in a water bath for temperature control are less expensive than vessels with jackets or coils, but much labor is required for handling them. Pressure vessels that

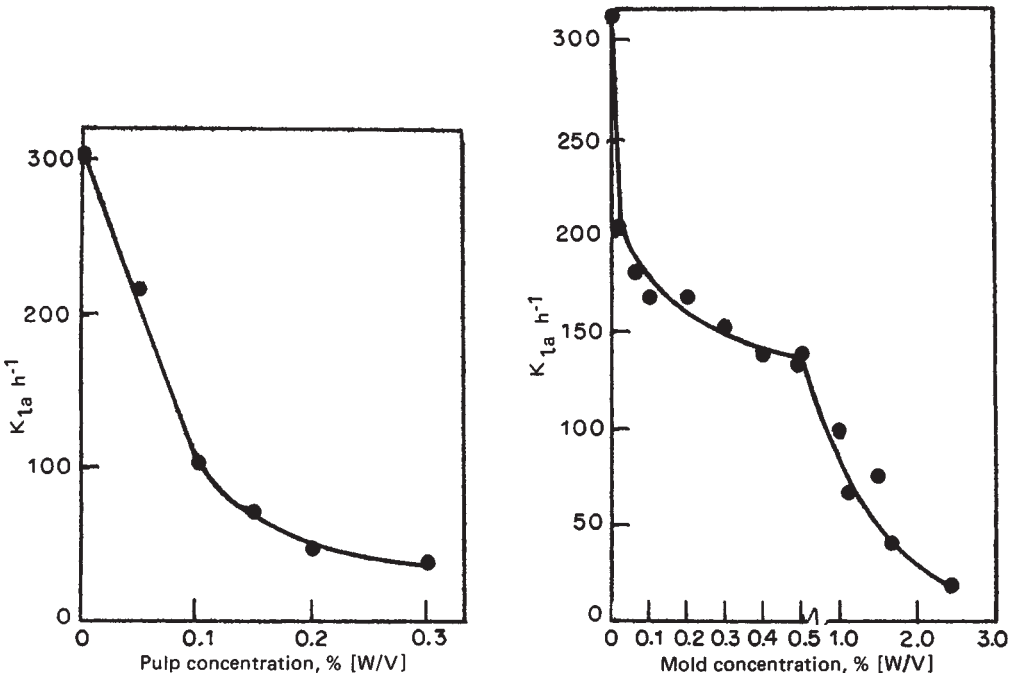


FIG. 24-16 Effect of solids on $K_l a$. Operating conditions: agitator speed, 800 r/min; air flow, 2.5 min. [*M. R. Brierly and R. Steel,* Appl. Microbiol., **7,** *57 (1959). Courtesy of American Society for Microbiology.*]

are sterilized in place are more convenient, but initial investment is high. Judgement is needed to select the most economical equipment and to plan for cost-effective experimentation.

A suitable means of scale-up for aerobic processes is to measure the dissolved oxygen level that is adequate in small equipment and to adjust conditions in the plant until this level of dissolved oxygen is reached. However, some antibiotic fermentations and the production of fodder yeast from hydrocarbon substrates have very severe requirements, and designers are hard-pressed to supply enough oxygen.

Older methods of fermentation scale up insisted on geometric similarity based on proportional physical dimensions. It was thought that applying the same power per unit volume as in the pilot equipment would give an equivalent process performance in large fermenters. Antibiotic fermentations aim for mixer power in the range of 0.2 to 4 Kw/m (0.1 to 2 HP/100 gal). As mixing devices have areas (dimensions squared) to supply a volume (dimensions cubed), methods based on dimensional similarity are fundamentally unsound. Scale-up based on equivalent oxygen transfer coefficient $K_l a$ has been reasonably successful.

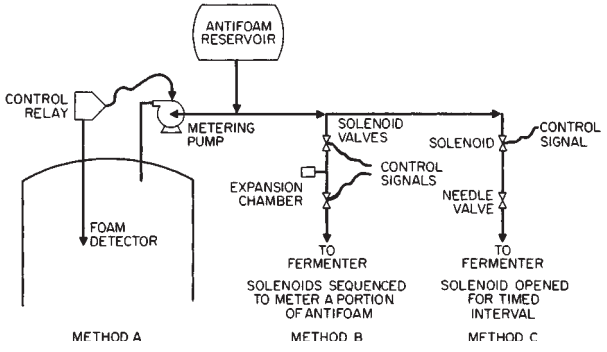


FIG. 24-17 Antifoam systems.

Impeller Reynolds number and equations for mixing power for particle suspensions are in Sec. 5. Dispersion of gasses into liquids is in Sec. 14. Usually, an increase in mechanical agitation is more effective than is an increase in aeration rate for improving mass transfer.

Other scale-up factors are shear, mixing time, Reynolds number, momentum, and the mixing provided by rising bubbles. Shear is maximum at the tip of the impeller and may be estimated from Eq. (24-5), where the subscripts *s* and *l* stand for *small* and *large* and *Di* is impeller diameter [R. Steel and W. D. Maxon, *Biotechnol. Bioengr.,* **4,** 231 (1962)].

$$S_s = S_l \left(\frac{Di_s}{Di_l} \right)^{1/3} \tag{24-5}$$

Some mycelial fermentations exhibit early sporulation, breakup of mycelium, and low yields if the shear is excessive. A tip speed of 250 to 500 cm/s (8 to 16 ft/s) is considered permissible. Mixing time has been proposed as a scale-up consideration, but little can be done to improve it in a large fermenter because gigantic motors would be required to get rapid mixing. Culturing cells from plants or animals is beset by mixing problems because these cell are easily damaged by shear.

Constant Reynolds number is not used for fermentation scale-up; it is only one factor in the aeration task. This is also true for considering the impeller as a pump and attempting scale-up by constant momentum. As mechanical mixing tends to predominate over bubble effects in improving aeration, scale-up equations including bubble effects have had little use.

Fermentation biomass productivities usually range from 2 to 5 g/(l·h). This represents an oxygen demand in the range of 1.5 to 4 g O/(l·h). In a 500-m fermenter, this means achievement of a volumetric oxygen transfer coefficient in the range of 250 to 400 h^{-1}. Such oxygen-transfer capabilities can be achieved with aeration rates of the order of 0.5 VVM (volume of air at STP/volume of broth) and mechanical agitation power inputs of 2.4 to 3.2 Kw/m (1.2 to 1.6 HP/100 gal).

Often heat removal causes design problems for scale-up. Mechanical agitation coupled with a metabolic heat from the growing biomass

overwhelms cooling capacity of a large fermenter with only a jacket. External circulation through a heat exchanger or extensive coils inside the fermenter must be used. In highly viscous fermentations, internal cooling coils are usually not desirable because of interference with mixing patterns. Numerous schemes exist for heat removal in large fermenters such as half-coil baffles (plate coils) and draft tubes. Heat removal limits the size of packed-cell bioreactors. There is also a serious problem of gas evolution for bioreactors when the cells are immobilized with a membrane or by retention in a gel because the gas can rupture the structure.

Evaporation of medium provides a little cooling. The inlet air to particulate filters must not be near saturation because condensation of moisture on the filter medium mobilizes contaminating microorganisms so that their chances of penetration are greatly increased. Sometimes humidified air is used, and the filter unit is heated to prevent condensation. However, this is common only for small equipment where the extra operations are relatively easy to install and maintain.

Once a plant is built, the conditions of agitation, aeration, oxygen transfer, and heat transfer are more or less set, and sterilization cycles are defined. Those environmental conditions achievable in plant-scale equipment should be scaled down to the pilot plant and laboratory equipment (shaken flasks) to insure that results can be translated.

Sterilization Some old, traditional fermentations such as those for alcohol and pickles are conducted by organisms that are hardy and help their own cause by creating conditions that are unfavorable for competitors. Yeasts, for example, lower pH by producing acids from sugars, and tolerance to alcohol is another powerful advantage that allows their domination. Nevertheless, modern factories use aseptic techniques or extreme care to minimize contamination that can jeopardize product quality by affecting taste, texture, aroma, or appearance. Bioprocesses such as tissue culture to produce vaccines are very easily contaminated because there is an abundance of nutrients and no inherent protection against foreign organisms. Thus, bioprocesses range from relatively good self-protection to practically none; the value of the product and the need for quality control determine the extent to which precautions must be taken. Contamination in the practical sense is statistical in that foreign organisms can be present but may not propagate rapidly enough to damage the run. Good defense against contamination is relatively inexpensive, while absolute protection is impossible and attempts to achieve it can be inordinately costly. The production of agents for biological warfare takes extreme pains to keep the organisms away from the workers, yet people operating the fermentations are occasionally killed. The most expensive and best protected industrial fermentations are sometimes contaminated. Sterilization and aseptic techniques to keep bioprocesses uncontaminated can be crucial.

Common ways of sterilization are removal of microorganisms by filtration or killing them with heat or chemicals. Sterilization by filtration follows a standard unit operation that is covered in Sec. 18. The differences for biochemical engineering are: (1) the filter medium and the downstream lines are steamed at a pressure where the temperature kills all organisms and spores; (2) the sizes of the particles being removed are in the micrometer range; and (3) the filter medium should be reusable and not degraded by repeated heating.

Sterilization by Filtration Air is almost always sterilized by filtration. The alternative of heating to sterilize has been successful for small installations, but large equipment for heating an air stream to sterilizing temperatures has not been sufficiently reliable. While it seems simple enough to maintain a section of the air-supply pipeline at high temperature, automatic control is needed to adjust for varying heat transfer as flow rate changes, and an air cooling section is needed to prevent excessive heat load on the fermenter. Furthermore, energy costs are now much higher than when heating seemed a promising alternative to filtration. For exit gases from a fermentation that has hazardous organisms, heating is a reasonable precaution, and cost is not the key factor. A clever heating method failed in full-scale testing. The air was compressed to raise its temperature by the Joule-Thompson effect, but the method was abandoned because several batches became contaminated. Any flow system for heat sterilization is crippled by process upsets because a slug of material can have inadequate temperature or exposure time for killing.

Sterilization of liquids by filtration has performed very well since the advent of membrane filters of small pore size. When heat can damage the ingredients, filtration is an ideal choice. However, the extra handling and equipment mitigate against filtration because heat sterilization of a batch is easy and relatively inexpensive. A tank must be steam-sterilized anyway, so it is convenient to fill it first and sterilize the contents as well. When some constituents must not be subjected to heat, it is customary to sterilize the rest of the medium with heat and to filter concentrated solutions of the delicate ingredients. Very large vessels can have insufficient heat-transfer surface; the tank is sterillized empty, and the medium is sterilized by flow through a continuous sterilizer.

The magnitude of the air sterilization problem is seen from the usual needs of a highly aerobic fermentation where roughly 1 volume of air per volume of medium per minute may be used. For a factory with 20 fermenters of 100,000 l (3500 ft^3) each, 2 million l/m (70,000 ft^3/m) of air is handled. Very large compressors are used, and at least two are required so that one can be down for maintenance.

Fibrous or particulate filters are not important anymore because membrane filters are relatively compact and perform very well. For filtration by straining, there is an intermediate air velocity at which filtration efficiency is a minimum because different collection mechanisms predominate at different ranges of velocity. At low velocities, diffusional and electrostatic forces on the particle are important, and increased velocity shortens the time for them to operate. At high velocities, inertial forces that increase with air velocity come into play; below a certain air velocity, their effect on collection is zero. Surges or brief power failures could change velocity and collection efficiency.

Membrane filters for air sterilization are reliable and relatively small. Membranes are quite efficient for filtering air and tend to capture particles larger than the pore size. To ensure safety, a pore size of 0.2 to 0.3 micrometers is recommended. Hydrophilic membranes should not be used because moisture is held tightly in their pores and not dislodged unless quite high pressure drops are created across the membrane. Moisture tends to drain from hydrophobic membranes and collect in a sump. Sizing of a membrane unit for air filtration is based on the number of cartridges needed. Only 60 percent of the available pressure drop should be used in the calculation to allow for increased resistance as particles collect on the membrane. Figure 24-18 shows membrane cartridges in parallel in a housing.

Sterilization of Media First-order kinetics may be assumed for heat destruction of living matter, and this leads to a linear relationship when logarithm of the fraction surviving is plotted against time. However, nonlogarithmic kinetics of death are quite often found for bacterial spores. One model for such behavior assumes inactivation of spores via a sensitive intermediate state by the mechanism:

$$C_r \rightarrow C_s \rightarrow C_d \qquad (24\text{-}6)$$

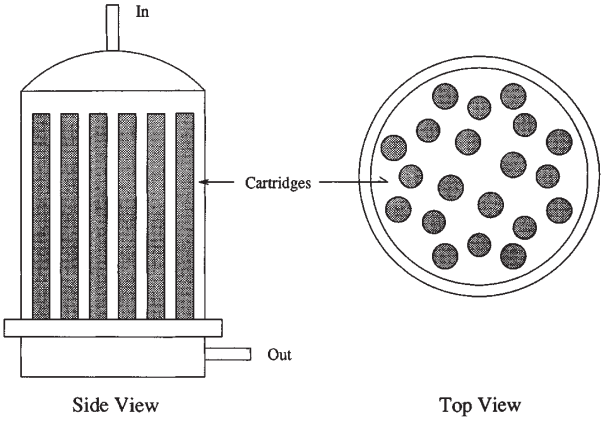


FIG. 24-18 Sketch of housing and membrane cartridges for air filtration. Typical cartridges are 76 cm long and 7.36 cm in diameter of polyvinylidene difluoride with 0.22-μm pores.

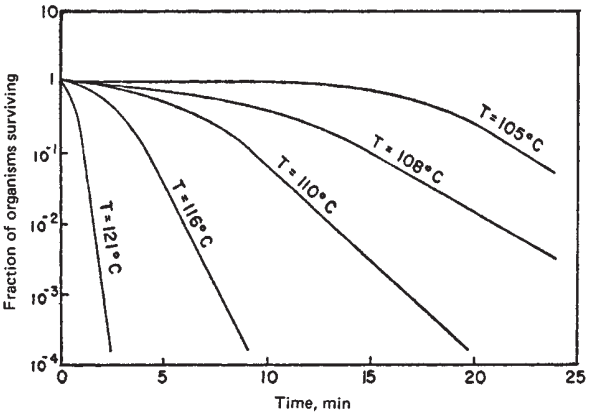


FIG. 24-19 Typical death-rate data for bacterial spores (*B. stearothermophilus*). To convert °C to °F, multiply by 1.8 and add 32 (*Wang et al.,* Fermentation and Enzyme Technology, *Wiley-Interscience, New York, 1979, p. 140.*)

where C_r, C_s, and C_d are concentrations of resistant, sensitive, and dead spores, respectively. Typical plots are in Fig. 24-19.

Relative thermal resistance for the different types of microorganisms encountered in typical environments associated with fermentation broths is shown in Table 24-3. Bacterial spores are far more resistant to moist heat than are any other type of microbial contaminants; thus, a sterilization cycle based on the destruction of bacterial spores should destroy all life.

TABLE 24-3 Relative Resistance to Killing by Moist Heat

	Relative resistance
Vegetative bacteria or yeast	1.0
Bacterial spores	3,000,000
Mold spores	2 to 10
Virus and bacteriophage	1 to 5

As predicted by the Arrhenius equation (Sec. 4), a plot of microbial death rate versus the reciprocal of the temperature is usually linear with a slope that is a measure of the susceptibility of microorganisms to heat. Correlations other than the Arrhenius equation are used, particularly in the food processing industry. A common temperature relationship of the thermal resistance is *decimal reduction time* (DRT), defined as the time required to reduce the microbial population by one-tenth. Over short temperature intervals (e.g., 5.5°C) DRT is useful, but extrapolation over a wide temperature interval gives serious errors.

The activation energy (E) associated with microbial death is larger than the thermal inactivation of chemical compounds in fermentation broths (see Table 24-4). Thus by sterilizing at high temperatures for short times (HTST), overcooking of nutrients is minimized.

TABLE 24-4 Various Activation Energies for Thermal Destruction

	Activation energy, cal/mol
Folic acid	16,800
d-Panthothenyl alcohol	21,000
Cyanocobalamin	23,100
Thiamine hydrochloride	22,000
Bacillus stearothermophilus	67,700
Bacillus subtilus	76,000
Clostridium botulinum	82,000
Putrefactive anaerobe NCA 3679	72,400

To convert calories per mole to British Thermal Units, multiply by 1.8.

Batch Sterilization Assuming that the presence of one single contaminating organism could cause ultimate failure of the desired fermentation, it is necessary to assign some probability of success. For example, if one contaminated fermentation per thousand can be tolerated, the design calculation for the sterilization cycle should use 0.001 organisms per fermentation. However, in batch sterilization, the heating, holding, and cooling portions of the cycle all contribute toward the reduction of the microbial contaminants. Furthermore, the specific death-rate constant varies because the temperature of the medium changes. Therefore, the design criterion total is composed of

$$\nabla \text{ total} = \nabla \text{ heating} + \nabla \text{ holding} + \nabla \text{ cooling}$$

$$\nabla \text{ heating} = \ln \frac{N_0}{N_1} = A \int_0^{t_1} \exp\left(-\Delta E/RT\right) dt \tag{24-7}$$

$$\nabla \text{ holding} = \ln \frac{N_1}{N_2} = A \int_0^{t_2} \exp\left(-\Delta E/RT\right) dt \tag{24-8}$$

$$\nabla \text{ cooling} = \ln \frac{N_2}{N} = A \int_0^{t_3} \exp\left(-\Delta E/RT\right) dt \tag{24-9}$$

Other parameters affecting the temperature profile include the viscosity of the medium and amount of suspended solids or insoluble materials such as vegetable oils that can foul heat-transfer surfaces. Releasing part of the pressure after the holding period gives flash cooling. The temperature-time profile during the cooling portion of the sterilization cycle includes effects of cooling coils or the fermenter jacket and evaporative cooling if sterile air is injected to remove heat. Most of the sterilization is derived from the holding portion of the cycle; the cooling cycle contributes little to the overall process. An extremely long heating cycle should be avoided because its contribution towards microbial destruction is far outweighed by its detrimental biochemical effects.

Continuous Sterilization Continuous sterilization permits short detention times at high temperature to avoid overcooking and has potential for improvement in yield. Tubular or plate-and-frame heat exchangers in a system for continuous sterilization provide economical heat exchange between process streams. However, direct injection of steam offers almost instantaneous heating to the sterilization temperature but wastes energy because heating and cooling are not integrated. Steam injection has no heating surface to foul.

In the holding section of a continuous sterilizer, correct exposure time and temperature must be maintained. Because of the distribution of residence times, the actual reduction of microbial contaminants in the holding section is significantly lower than that predicted from plug flow assumption. The difference between actual and predicted reduction in viable microorganisms can be several orders of magnitude; therefore, a design based on ideal flow conditions may fail.

Cell Culture Single plant and animal cells are much larger than microbial cells and are easily damaged by shear due to intense agitation. Standard stirred tank bioreactor designs tend not to work well for undifferentiated plant and animal cells. Attempts to substitute paddle and spiral agitators has proven successful in some cases, but shear can still cause a morphological change in the structure of the cells. Usually, single cells and cellular aggregates tend to be smaller and produce significantly less secondary metabolites with improper agitation. Airlift reactors may work well, and cultured cells tend not to have severe oxygen requirements. There has been a thrust for new systems that can maintain absolute sterility without depending on antibiotics that can mask the slow development of a low-grade infection in a culture and can affect the metabolism of cultured cells in subtle ways that cannot always be predicted.

Cells that must attach to a surface can be grown on spongy polymers, arrays of thin tubing or hollow fibers, stacks of thin plates, or microscopically small beads called microcarriers. Damage from shear can be a serious problem; thus, aeration systems cannot employ the vigorous mixing that aids mass transfer in microbial processes. Airlift bioreactors have been developed that are tapered instead of being cylindrical with a central draft tube. Above a zone of intense aeration are the suspended cells circulating with little more mixing than would result from Brownian motion.

Improvements in fermentation include microcarriers that not only provide support for anchorage-dependent cells but also aid in harvesting at the end of a run. While microcarriers based on dextran, polystyrene and polyacrylamide beads have been widely used in the past, new materials for microcarriers make separating cells from their growth medium easier. Some are made of collagen that is detached from the cells by immersion in dilute collagenase. However, since some collagen can be left in solution, downstream processing can be made difficult. An alternative is to use plastic beads coated with collagen. The plastic can be easily separated after the cells are released enzymatically. Another alternative is glass-coated particles that induce attachment of the cells' long slender filopodia. At the end of a process, a brief incubation in dilute trypsin gently removes the cells from the beads.

Supplying sufficient oxygen can be difficult when dealing with differentiated plant tissues such as root cultures that can reach lengths of several decimeters and can be highly branched and complex structurally. In this case, mechanical agitation is impractical because the mass of roots can occupy approximately 50 percent of the reactor volume. Alternatives are bubble columns, rotating drums, and trickle bed reactors where the medium is recycled and sprayed over the column of roots.

Because of the differences in primary and secondary metabolism, a reactor may have a dual-stage fed-batch system. In other words, fed-batch operation optimizes growth with little or no product formation. When sufficient biomass has accumulated, a different fed-batch protocol comes into play.

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PRODUCT RECOVERY

Although most of the purification equipment in a large biotechnological factory is the same as that used throughout the chemical process industries, there are fewer separations in which the product reaches elevated temperatures. Most biochemicals are destroyed if heated. Recovery of products from the bioprocess fluid can be more difficult and expensive than all of the previous steps. The ratio of recovery costs to cost of creating the product can range from about one to more than ten because the investment for the recovery facilities may be several times that for the fermenter vessels and their auxiliary equipment. As much as 60 percent of the fixed costs of fermentation plants for organic acids or amino acids is attributable to the recovery section. The costs for recovery of proteins based on recombinant DNA techniques are particularly high.

Research and development for better recovery of existing products may provide diminishing returns as time passes, and some companies focus on new products. Government regulations are different for drugs that are sold in very nearly pure state and for biologicals that may be ill-defined. Little paperwork is required for a process improvement for a pure drug. For biologicals intended for humans, securing government approval makes it unwise to modify the recovery process except when the potential savings are very great. The extensive and expensive testing and validation of such therapeutic agents is keyed to the processes for making and purifying them. Only trivial changes are permitted; otherwise the testing must be repeated. Market forces make it important to have a new product tested and ready for sale as quickly as possible, but this usually means that the process has not been optimized. Whereas competition and process improvements resulted in remarkable lowering of prices in the past, the regulations now discourage investment in process development other than at the early stages prior to submission of the documents for government approval.

Certain products (e.g., inclusion bodies) are contained inside the cells and are not released or only partially released to the medium. It may be possible to flush impurities from the cells before breaking them to get the product. Cell disruption is a unit operation peculiar to biochemical engineering. The equipment, however, may be borrowed from other industries. Colloid mills and shear devices used for manufacturing paint and other products effectively rupture walls of many types of cells. Cells with high resistance to shear can be passed through the unit several times, but heat generation from the process can cause loss of product. Shear alone can denature sensitive proteins. Ultrasonic energy is commonly used on a small scale for cell disintegration but is impractical for large batches. Grinding with sand or beads, high-pressure pumping through a tiny orifice, freezing and thawing, dessication, adding lytic enzymes, inducing autolysis with a chemical such as chloroform, and various means of creating shear are alternative or synergistic means of rupturing cells. There are encouraging results with special mutants of cells with impaired ability to form cell walls at temperatures slightly above their normal growth temperatures. When shifted to the elevated temperature, cell division gives damaged walls and lets the cell contents leak out. The bioprocess operates at its optimum temperature until the temperature is raised shortly before harvest. Cells that form at the elevated temperature release their contents easily.

Whenever possible, the fermentation fluid goes directly to ion exchange, solvent extraction, or some other step. However, prior removal of biological cells and other solids is usually necessary. Centrifugation can be considered, but rotary drum filters with string discharge are commonly used. In the past, large amounts of filter aid were added because many fermentation broths are slimy and hard to filter. Present practice employs polymeric bridging agents to agglomerate the solids. This allows good filtration with only small amounts of filter aid.

The most popular steps for recovery are ion exchange or solvent extraction because selectivity is good, costs are reasonable, and large scale is feasible. Unfortunately, some biochemicals neither exchange ions nor extract well. These and other purification steps can be affected by modifications in fermentation. Adding excess lipids or antifoam oils to a fermentation can aggravate emulsion problems for solvent extraction or impair ion exchange by coating the resin. Stability of biochemical products can be troublesome. For example, penicillin fermentation broth is acidified just prior to contact with the extracting solvent because low pH causes very rapid destruction of penicillin in water. The most popular immiscible solvent is methylisobutylketone (MIBK); halogenated hydrocarbons are avoided because of their hazard for humans. Penicillin is extracted back into an aqueous phase at pH 7.5 to 8 using bicarbonate as a buffer because harsher agents are difficult to control. The Podbelniak design of centrifuge (see Sec. 15) is widely used in the United States for extraction of fermentation broths, while the Westphalia design is common in Europe. Countercurrent flow through a centrifuge should result in more than one equilibrium contact, but emulsions may carry product into the phase being wasted. Lead-and-trail operation of the centrifuges can improve yields. Extraction back into water is seldom troubled by emulsions, and DeLavalle separators work well.

Some products are precipitated from the fermentation broth. The insoluble calcium salts of some organic acids precipitate and are collected, and adding sulfuric acid regenerates the acid while forming gypsum (calcium sulfate) that constitutes a disposal problem. An early process for recovering the antibiotic cycloserine added silver nitrate to the fermentation broth to precipitate an insoluble silver salt. This process was soon obsolete because of poor economics and because the silver salt, when dry, exploded easily.

Of the various types of purification steps based on sorption to a

solid phase, ion exchange is the most straightforward. See Sec. 22 for a discussion of techniques. Ion-exchange resins actually adsorb Vitamin B_{12} well instead of exchanging it. Carbon adsorption has considerable importance to biochemical engineering, primarily for the removal of traces of colored impurities. When neither solvent extraction nor ion exchange can be used as the primary concentration/purification step because of the chemical properties of the desired product, an alternative may be adsorption on carbon. Although carbon adsorption may be unselective and low in capacity, it can provide a roughing step to get the purification scheme started.

Isolation procedures for many biochemicals are based on chromatography. Practically any substance can be selected from a crude mixture and eluted at relatively high purity from a chromatographic column with the right combination of adsorbent, conditions, and eluant. For bench scale or for a small pilot plant, such chromatography has rendered alternate procedures such as electrophoresis nearly obsolete. Unfortunately, as size increases, dispersion in the column ruins resolution. To produce small amounts or up to tens of kilograms per year, chromatography is an excellent choice. When the scale-up problem is solved, these procedures should displace some of the conventional steps in the chemical process industries.

Affinity chromatography uses ligands with high specificity for certain compounds. There are several types of affinity that can be employed: antigen-antibody, enzyme-substrate, enzyme-cofactor, chelation with metal ions, or special biochemical attractions such as the protein avidin for the vitamin biotin. Numerous purifications have been devised wherein affinity chromatography is able to isolate quite pure product from a very crude mixture. Expensive affinity agents are regenerated and reused many times. In some cases, the attraction is so strong that the adsorbent can be added batchwise. This scales up well but is less convenient than column operations in terms of collection, elution, and regeneration of the affinity agent.

Conventional elution chromatography has the serious disadvantage of dilution, and usually a concentration step must follow. The technique of displacement chromatography circumvents dilution and may even result in an eluant more concentrated than the feed. A displacer compound breaks the desired product from the chromatographic material sharply, and a column heavily loaded with several biochemicals will release them one at a time depending on their adsorption equilibria. However, the displacers tend to be expensive and can be troublesome to remove from the product.

A number of water-soluble polymers will cause phase separation when present together at concentrations of a few percent. The most widely used polymers are polyethylene glycol (PEG) and dextran. Proteins, other macromolecules, and cell components such as mitochondria distribute in the phases or collect at the interface. Proteins are destabilized at organic solvent/water interfaces, but when each solvent is water, the interfacial tension is negligible. Some salts such as potassium phosphate will also induce phase separation when a polymer is present, but the salt concentration must be high. Two-phase aqueous systems provide a mild method for purification of proteins, and scale-up to large volumes presents no engineering problems. The polymers can have functional groups that improve distribution coefficients of the biochemical products, but the costs for these polymers are high. Although highly promising, two-phase aqueous methods are used only for valuable products because the cost of the polymers is too high and they are not easily recovered for reuse. Another drawback is distribution coefficients not far from 1 for most proteins; several extraction stages are needed to get acceptable yields when the distribution coefficients are unfavorable.

Surface-active agents and liquids immiscible in water can form tiny dispersed units called reverse micelles. These can extract biochemicals from water or permit complexing or reacting in ways not possible in simple aqueous systems.

Crystallization is the preferred method of forming many final products because very high purification is possible. High purity antibiotic crystals can be produced from colored, rather impure solutions if the filter cake is uniform and amenable to good washing to remove the mother liquor. When a sterile pharmaceutical product is desired, crystals are formed from liquid streams that have been sterilized by filtration.

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PROCESS MODELING

It is generally assumed that properties of very large numbers of cells can be treated as continuous functions having average properties because there are so many cell divisions occurring that the overall rates follow smooth curves. There is an exception in which the cells can all be induced to divide at the same time because events such as illumination or temperature changes slow or halt a step in division. The cells can be triggered to proceed together from that point with overall numbers that are stepwise with time. This is termed a *synchronous culture;* the steps are seldom distinct for more than a few generations unless the triggering event continues to be applied periodically.

Mass balances for common, unsynchronized batch culture give:

$$\frac{dX}{dt} = \mu X - K_d X \tag{24-10}$$

$$\frac{dS}{dt} = -\frac{\mu X}{Y} \tag{24-11}$$

$$\mu = f(S) \tag{24-12}$$

Various functional relationships between μ and S have been proposed, but the Monod equation is used almost exclusively:

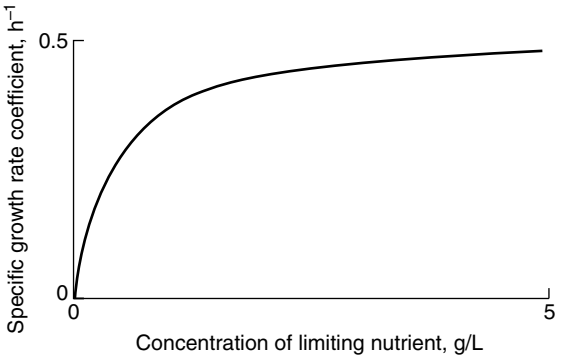


FIG. 24-20 Plot of the Monod equation.

$$\mu = \mu_{max} \times \frac{S}{K_s + S} \tag{24-13}$$

A graph of the Monod equation is shown as Fig. 24-20.

The death rate coefficient is usually relatively small unless inhibitory substances accumulate, so Eq. (24-10) shows an exponential rise until S becomes depleted to reduce μ. This explains the usual growth curve (Fig. 24-21) with its lag phase, logarithmic phase, resting phase, and declining phase as the effect of K_d takes over.

Structured Models Meaningful detail can be added to culture models in several ways. Cells can be compartmentalized according to biochemical functions, and the components can interact. For example, there can be a group of equations for carbohydrate metabolism, a group for protein synthesis, another for nucleic acid synthesis, and so on. This permits a much more intricate description of cell activities but at the expense of having so many rate constants that assigning values to them may end up as guesswork. For cells with distinct life cycles, a structured model may have compartments corresponding to each stage in the cycle. In addition, each compartment may be subdivided into the biochemical functions mentioned above. Such complicated models have had limited practical use but have great value for directing research toward areas where information is lacking.

Continuous Culture Continuous culture has been a goal of bioengineers for several decades because batch culture has inherent down time for cleaning and sterilization and long lags before the organisms enter a brief period of high productivity. Continuous runs can last many weeks, but there must be stoppages for cleaning and maintenance. Bacteria may foul surfaces to a small extent, but molds tend to form thick coatings on the shaft, coils, and any protuberances in the fermenter after several weeks of continuous cultivation, that seriously impair mixing and mass transfer.

The nutrition and the product mix can be advantageously manipulated as functions of dilution rate. A serious problem, however, is instability of the culture itself. There is a tendency to revert to less productive strains that quickly replace the finely tuned mutants that achieve high titers of product. The main successes with continuous fermentation have been with rugged strains that are producing either cell mass for cattle feed or a simple enzyme or metabolite. When a single stage is used for a product that is elaborated from cells that are not growing, it is difficult to optimize simultaneously cell growth, product production, and efficient use of substrates.

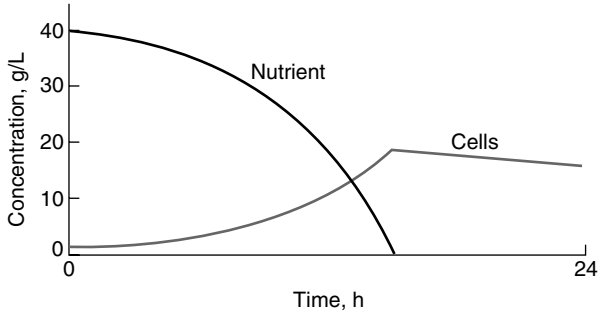


FIG. 24-21 Microbial growth curve. $dx/dt = \mu X - K_d X$; $ds/dt = -\mu X/Y$; $\mu = \mu_{max} S/(K_s + S)$; $\mu_{max} = 0.35$; $K_d = 0.025$; $K_s = 12.0$ mg/L; $Y = 0.48$.

In view of its few industrial applications, continuous culture gets a disproportionate amount of attention from academicians. As a research tool, batch culture suffers from changing concentrations of products and reactants; varying pH and redox potential; and a complicated mix of growing, dying, and dead cells. Data from continuous cultures are much easier to interpret because steady states are achieved or there are repeatable excursions from steady state. The usual explanations for limited use of continuous culture in industry are: culture instability, difficulty of maintaining asepsis, insufficient knowledge of microbial behavior, and reluctance to convert existing factories. Overall cost savings can be relatively small for continuous cultivation because productivity of the bioreator is not very important compared to high product concentration. Another factor is the cost of each research station. Rapid progress in research and development requires multiple vessels for screening many variables, but there are usually only one or two continuous fermenters in the lab or pilot plant because the cost of pumps, reservoirs, sterilizers, and controls is relatively high.

Conventional means for continuous culturing are the chemostat in which nutrient is fed to a reactor at constant rate and the turbidostat that employs feedback control of pumping rate to maintain a fixed turbidity of the culture. Another alternative with feedback control of a nutrient or product concentration has been termed *auxostat, nustat,* or *nutristat.* Proportional control of the pumping rate is desirable because continuous cultures can have oscillatory responses induced by turning the feed pump on or off. A chemostat tends to be unstable and erratic at dilution rates that approach the maximum specific growth rate of the organisms. This is explained by the adjustment of growth rate to nutrient concentration in the region where a small change in dilution rate equates to a big change in nutrient concentration. An auxostat has little advantage over a chemostat at moderate dilution rates but is stable at the high dilution rates at which the chemostat is unreliable.

MATHEMATICAL ANALYSIS

The concept of a limiting nutrient is essential to the theory of continuous culture. There will only be exact stoichiometric balance of all the ingredients going into the cells when a very deliberate and time-consuming effort has been made to determine the details of cell nutrition. Even then, there may be a different balance if the growth rate is changed or kinetic rather than stoichiometric limitations may apply. The ingredient in short supply relative to the other ingredients will be exhausted first and thus limit cellular growth or product synthesis. The other ingredients may exhibit toxicity or influence cellular activities, but there will not be acute shortage as in the case of the limiting nutrient.

Mass balances for one vessel in a series of continuous fermenters give:

Rate of change = rate in − rate out + rate of production

or
$$\frac{V dX_n}{dt} = FX_{n-1} - FX + V\mu_v X_n \tag{24-14}$$

Dividing through by V and substituting $D = F/V$:

$$\frac{dX_n}{dt} = D(X_{n-1} - X_n) + \mu_n X_n \tag{24-15}$$

and
$$\frac{V dS_n}{dt} = FS_{n-1} - FS_n - \frac{V\mu_n X_n}{Y} - VMX_n \tag{24-16}$$

$$\frac{dS_n}{dt} = D(S_{n-1} - S_n) - \frac{\mu_n X_n}{Y} - MX_n \tag{24-17}$$

For a single vessel with sterile feed, this reduces to:

$$\frac{dX}{dt} = \mu X - DX \tag{24-18}$$

$$\frac{dS}{dt} = D(S_o - S) - \frac{\mu X}{Y} - MX \tag{24-19}$$

This is an old, familiar analysis that applies to any continuous culture with a single growth-limiting nutrient that meets the assumptions of perfect mixing and constant volume. The fundamental mass balance equations are used with the Monod equation, which has no time dependency and should be applied with caution to transient states where there may be a time lag as μ responds to changing *S*. At steady state, the rates of change become zero, and $\mu = D$. Substituting:

$$D = \mu_{max} \frac{S}{K_s + S} \tag{24-20}$$

and

$$S = \frac{DK_s}{\mu_{max} - D} \tag{24-21}$$

Solving for *X* gives:

$$X = DY \times \frac{S - S_o}{D + MY} = Y(S_o - S) \tag{24-22}$$

From these equations, the behavior of *X* and *S* as functions of dilution rate can be plotted as in Fig. 24-22.

The interesting features are: (1) *X* goes to zero and *S* reaches S_o as *D* approaches μ_{max}; (2) *S* is not a function of S_o when *D* is less than μ_{max}; (3) the maintenance coefficient is very important at low dilution rate but has little effect afterwards; and (4) S_o is never so high that μ_{max} can be reached, thus washout always occurs before μ_{max} and is a function of S_o.

Mixing has been shown to be critical at low dilution rates because uptake of substrate is extremely rapid for cells in a starved condition. Vigorous agitation is required in small vessels to insure homogeneous distribution of the feed; such intense agitation is probably impractical in large vessels, but good dispersion has been achieved by distributing the feed from many fine openings throughout the vessel.

It is easy to postulate advantages for multistage continuous culture but very difficult to conduct all of the research and development of the many parameters that should be optimized. Each stage could have its feed streams, control of pH and other conditions, and recycle of cells or fluids from other steps in the process. Not only are there many parameters to study for each stage, but changes in one stage can markedly affect other stages. It can be quite troublesome to get representative conditions and cultures in a given stage to begin research because of the complicated interactions with other stages. Time delays in lines and separators for recycling plus complexities from nonideal flow regimes cause a theoretical analysis to be faulty. An optimized multistage continuous fermentation system with recycle and control is a most difficult engineering feat, and the dynamics of microbial responses to upsets are poorly understood. Nevertheless, a three-stage continuous fermentation process is used in industry for the manufacture of a vitamin.

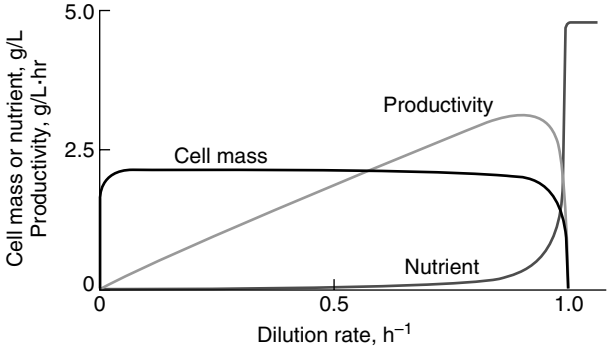


FIG. 24-22 Computer analysis of steady states in continuous culture; $\mu = 2.38$ h^{-1}; $S_o = 1100$ mg/l; $Y = 0.45$; $K_s = 35$ mg/l; $M = 0.05$.

COMPUTER AIDS FOR ANALYSIS AND DESIGN

Specialized programs make layout easy in the form of diagrams of the individual components and their interconnections. Often there are databases for thermodynamic properties as well as routines that will calculate approximate values for properties of the compounds handled in the factory. The programs save the engineer from many tedious calculations, and it is practical to investigate options for equipment sizes and operating conditions. Advice on selecting modeling software is available [Chan, W. K., J. F. Boston, and L. B. Evans, "Select the Right Software for Modeling Separation Processes," *Chem. Engr. Prog.*, **87,** 63–69 (1991)]. A partial list of programs is:

PRO/II from Simulation Sciences Inc., Fullerton CA

HYSIM from Hyprotech, Ltd., Calgary, Alberta; Houston TX; Whittier CA

CHEMCAD from Coade Engr. Software, Houston TX

DesignPFD from ChemShare, Houston TX

Aspen/SP from JSD Simulation Service Co., Denver CO

ELECTROSIM (processes dealing with dissociation and chemical reactions), from Real Time Simulation

POWERTRAN-PC, from Bigelow Systems

DataLogiX, from DataLogiX Formula Systems

G2, a bioprocess expert program with simulation and control from GENSYM, Cambridge, MA

BioPro Designer from Intelligen, Inc., Scotch Plains, NJ

PLANT CELL AND TISSUE CULTURES

Monod kinetics where the growth is limited by a single substrate can apply but only for specific stages of growth and not for the entire growth cycle of plant cells. An example of this is cells grown in a 14 l (0.5 ft^3) fermenter where the latter stages of growth were adequately described by the Monod equation but the initial stages were not. It is understandable that differentiated plant tissues with their distinct cellular characteristics may not be suited to a simple growth-rate expression. For example, root tissues have a meristematic stage where cells are actively dividing. This is followed by cells expanding and maturing to transport nutrients. Older cells may sequester certain nutrients until required by the younger cells and thus alter the availability of substrates.

A kinetic model originally derived by Nyholm is distinguished from Monod's model by the fate of a limiting substrate. Instead of immediate metabolism, the substrate in Nyholm's model is sequestered. The governing equations are:

$$\frac{dC_i}{dt} = v - \mu C_i \tag{24-23}$$

$$\mu = f(C_i) \tag{24-24}$$

$$v = \frac{1}{x}\frac{dS_i}{dt} \tag{24-25}$$

In these equations, μ = specific growth rate coefficient, *v* = specific rate of substrate uptake, *t* = time, *x* = biomass concentration, S_i = intracellular substrate, and C_i = concentration of intracellular substrate. Several examples where these equations can be applied include nitrogen limitations in *M. citrifolia* cultures and phosphate limited growth in *C. roseus, N. tabacum,* and *Papaver somniferum.*

The production of secondary metabolites has often been characterized using the classical equations of Leudeking and Piret. However, the complexities of plant cell and tissue cultures have led to revisions to this equation to include fresh cell weight and viability, cell expansion, and culture death phase. Therefore, the production model is written as the following:

$$\frac{dP}{dt} = \alpha V \frac{dX_d}{dt} + \beta V X_d + \frac{P}{V}\frac{dV}{dt} \tag{24-26}$$

where P = total intracellular product concentration, t = time, V = fraction of viable cells, and X_d = total dry cell weight. Furthermore, a and b represent the usual growth and nongrowth associated production constants, respectively. This type of model has been successfully applied to the production of ajmalicine and serpentine from *C. roseus* cell cultures. Similarly, the production of gossypol by *G. hirsutum* cell cultures used this type of production model but took into account the further metabolism of the phytoalexin due to the growth of new cells.

Because of the differences in primary and secondary metabolism, a reactor may have a dual-stage fed-batch system. In other words, fed-batch operation optimizes growth with little or no product formation. When sufficient biomass has accumulated, a different fed-batch protocol comes into play.

When the production of the secondary metabolites coincides with the death and general lysis of the cells, the recovery of the product is simply a matter of separation from the spent production solution downstream of the reactor. An example of this type of operation was initially used in Japan during the production of shikonin. However, if the secondary metabolites are stored in the vacuole of the cells and the cells remain viable but dormant during the production phase, then a permeabilizing agent such as dimethylsulfoxide (DMSO), detergents, proteins, and antibiotics may be employed in some cases in concentrations that make the cells leak product out but maintain cell viability. Success for this type of product recovery has been reported in *C. roseus, Datura innoxia,* and *Daucus carota* cell cultures.

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Recycle Separation and recycle of cells results in much longer residence times for the cells than for the fluid and permits relatively high cell concentrations. In waste treatment, the dilute feed leads to slow growth rates, so more rapid processing is attained through cell recycle to establish a higher population. A higher percentage of the cells may be dead in a recycle system because all are in a starved state. High rates of production are also important in industrial fermentations with cell recycle, and there is the added advantage of reusing cells instead of diverting expensive substrate to producing more cells.

In waste treatment with activated sludge units, organisms not associated with flocs are not collected and tend to leave the system as recycle increases the proportions of flocculating types. Recycle of collectible algae to outdoor ponds has profound influence on the population, but seasonal changes can develop small algae despite retention of large algae; thus, recycle fails as the few large algae die or escape collection.

Recycle of fermentation fluids has quite different objectives than those for cell recyle that aims for population control or greater productivity. Spent broths have leftover nutrients, so the recycling process can save on costs of nutrients and make up water while greatly reducing the volumes sent to waste treatment. Of course, total recycle is bad because undesirable materials build up in concentration and can poison the fermentation. This buildup determines the amount of recycle, but there may be purification steps to remove toxic substances. For example, glycerol is a by-product of alcohol fermentation, but its low volatility means that much is in the stillage from alcohol recovery. Its removal by a physical or chemical step would prevent accumulation in the fermenter by recycling. Alternatively, it could be metabolized by a special strain or mixed culture. Glycerol recovery from the recycle stream in the bioproduction of ethanol now competes with older processes for recovery in the oil and fat industries.

Figure 24-23 is a sketch of continuous culture with recycle. The symbols for flow rates and organism concentrations are F and X, respectively. Assuming perfect mixing and steady state so that the derivatives can be set to zero, mass balances lead to:

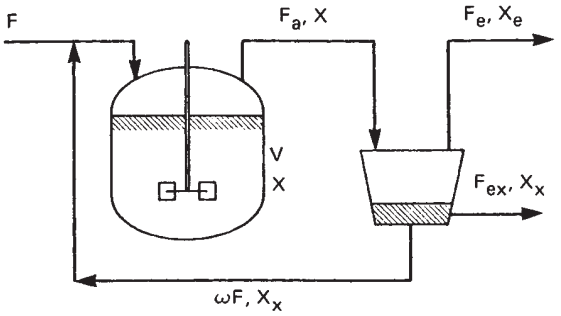


FIG. 24-23 Continuous culture with recycle. (*A. E. Humphrey, "Biochemical Engineering" in* Encyclopedia of Chemical Processing and Design, *vol. 4, July 1977, pp. 359–394.*)

$$\mu = D\left[1 + \omega\left(1 - \frac{1+\omega}{1+\omega-\frac{F_e}{F}}\right)\right] \qquad (24\text{-}27)$$

Without recycle, washout occurs when D is greater than μ_{max}, but recycle permits operation with D far greater than μ_{max}. A family of curves is shown in Fig. 24-24 for concentrations of cell mass and nutrient at different recycle ratios. The distinct differences from Fig. 24-22 with no recycle are obvious.

Mixed Cultures Mixtures of microorganisms characterize the processes shown in Table 24-5.

Processes for biological waste treatment have elective cultures, and the proportions of different species can shift dramatically in response to changing nutrition or physiological conditions. There is an interesting area of research on defined mixtures of microorganisms, but there has been little practical application of the results. The definitions of various interactions are in Table 24-6. These definitions are difficult to apply to real systems where there is highly complicated interplay among organisms that play various roles with respect to each other.

Two types of interaction, competition, and predation are so important that worthwhile insight comes from considering mathematical formulations. Assuming that specific growth-rate coefficients are different, no steady state can be reached in a well-mixed continuous culture with both types present because, if one were at steady state with $\mu = D$, the other would have μ unequal to D and a rate of change unequal to zero. The net effect is that the faster-growing type takes over while the other declines to zero. In real systems—even those that approximate well-mixed continuous cultures—there may be profound

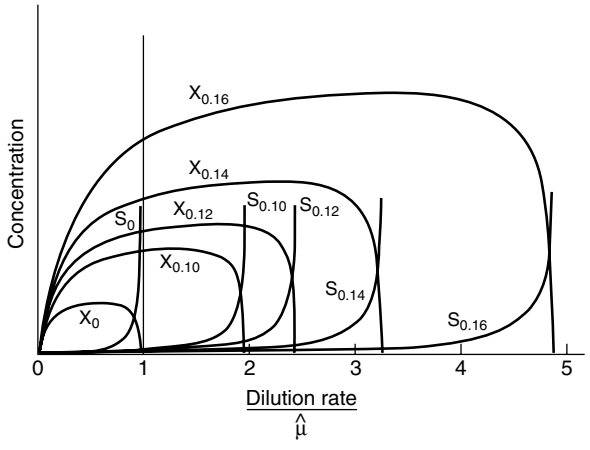


FIG. 24-24 Effect of recycle on steady-state concentrations of cell mass and limiting nutrient. 5-fold increase in cell concentration in separator. Subscripts denote fraction of cell concentrate recycled.

TABLE 24-5 Mixed Culture Processes

Process	Types of organisms
Commercial	
Alcoholic beverages	Various yeasts, molds, and bacteria
Sauerkraut	*L. plantarum* plus other bacteria
Pickles	*L. plantarum* plus other bacteria
Cheeses	Propionibacteria, molds, and possibly many other microorganisms
Lactic acid	Two lactobacillus species
Waste treatment	
Trickling filters	Zoogloea, protozoa, algae, fungi
Activated sludge	Zoogloea, *Sphaerotilus,* yeasts, molds, protozoa
Sludge digestion	Cellulolytic and acid-forming bacteria, methanogenic bacteria
Sewage lagoons	Many types from most microbial families

TABLE 24-6 Some Definitions of Microbial Interactions

Competition	A race for nutrients and space
Predation	One feeds on another
Commensalism	One lives off another with negligible help or harm
Mutualism	Each benefits the other
Synergism	Combination has cooperative metabolism
Antibiosis	One excretes a factor harmful to the other

changes in relative numbers of the various organisms present, but complete takeover by one type is extremely uncommon. Survival of a broad range of species is highly advantageous in natural systems because a needed type will be present should an uncommon nutrient (pollutant?) be added or the conditions change.

Prey-predator or host-parasite systems can be analyzed by mass balance equations:

$$\frac{dH}{dt} = \mu_H H - DH - KHP \tag{24-28}$$

$$\frac{dP}{dt} = \mu_P P - DP \tag{24-29}$$

$$\frac{dS}{dt} = D(S_o - S) - \frac{\mu_H H}{Y} \tag{24-30}$$

where H = the concentration of hosts (prey)
P = the concentration of predators
S = substrate concentration (food for prey)
K = a coefficient for killing

and μ_H and μ_P are Monod functions of S and H respectively.

Computer simulation of these equations is shown in Fig. 24-25. Real systems do have this type of oscillating behavior, but frequencies and amplitudes are erratic.

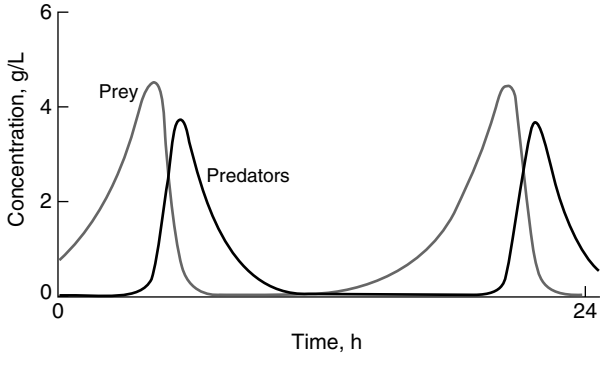


FIG. 24-25 Computer simulation of prey-predator kinetics.

Another interaction with grave consequences is attack on a species by a phage (microbial virus) that is usually highly specific. Infection of a cell by a virulent phage results in the production of 10 to several hundred new phage particles as phage nucleic acid takes over control of cellular activities. The cell disintegrates and releases phage that infect other cells to reach high phage titers quickly. A few cells of the host species may be resistant to phage; such resistance can be acquired through mutation. These cells have fewer competitors and may thrive. However, mutations also occur in phage, so highly complicated behavior occurs as the hosts mutate and mutate further as the phage mutates to counter host resistance.

Commercial fermentation groups usually maintain different strains of cultures suitable for production so that phage attacks can be thwarted by substituting a nonsusceptible culture. After a period of time for the phage to dissipate, it may be possible to return the most desirable production strain.

Bioprocess Control An industrial fermenter is a fairly sophisticated device with control of temperature, aeration rate, and perhaps pH, concentration of dissolved oxygen, or some nutrient concentration. There has been a strong trend to automated data collection and analysis. Analog control is still very common, but when a computer is available for on-line data collection, it makes sense to use it for control as well. More elaborate measurements are performed with research bioreactors, but each new electrode or assay adds more work, additional costs, and potential headaches. Most of the functional relationships in biotechnology are nonlinear, but this may not hinder control when bioprocess operate over a narrow range of conditions. Furthermore, process control is far advanced beyond the days when the main tools for designing control systems were intended for linear systems.

Many of the sensor problems such as those with steam-sterilizable pH electrodes and dissolved oxygen probes have been solved. Perhaps the most important factor for bioprocessing is the concentration of organisms, but there is no practical method for continuous measurement. Samples of the process fluid must be filtered and dried to get the mass concentration of cells. Numbers can be obtained by direct counting with a microscope or by counting the colonies that form when samples are cultured with nutrient medium in Petri dishes. In lieu of direct measurement, many other ways to estimate cell concentration are tried. Turbidity of the culture fluid can be correlated with cell concentration, but properties and calibration change during the process, and the optical surfaces of the sensors tend to become fouled. Alternatives such as measuring electrical conductivity or capacitance of the fluid sometimes are useful but often are suited only to specific cases. Indirect methods such as measuring protein produced by cells or monitoring nucleic acids are reported, but their proportionality to cell mass may vary during the fermentation. An important advance was made by developing computer models that can interpret measured variables to calculate cell mass or product concentration that may be difficult or impractical to measure on-line.

Mounting electrodes in a bioreactor is costly, and there is an additional contamination risk for sensitive cell cultures. Some other sensors of practical importance are those for dissolved oxygen and for dissolved carbon dioxide. The analysis of gas exiting from a bioreactor with an infrared unit that detects carbon dioxide or a paramagnetic unit that detects oxygen (after carbon dioxide removal) has been replaced by mass spectrophotometry. Gas chromatographic procedures coupled with a mass spectrophotometer will detect all the volatile components.

A useful index of process performance is the oxygen uptake rate, OUR, that is calculated from the difference in oxygen concentration of the inlet air and the exiting gas. Also important is the respiration ratio defined as the carbon dioxide evolved divided by the oxygen consumed.

Although dynamic responses of microbial systems are poorly understood, models with some basic features and some empirical features have been found to correlate with actual data fairly well. Real fermentations take days to run, but many variables can be tried in a few minutes using computer simulation. Optimization of fermentation with models and real-time dynamic control is in its early infancy; however, bases for such work are advancing steadily. The foundations for all such studies are accurate material balances.

The common indices of the physical environment are: temperature, pressure, shaft power input, impeller speed, foam level, gas flow rate, liquid feed rates, broth viscosity, turbidity, pH, oxidation-reduction potential, dissolved oxygen, and exit gas concentrations. A wide variety of chemical assays can be performed; product concentration, nutrient concentration, and product precursor concentration are important. Indices of respiration were mentioned with regard to oxygen transfer and are particularly useful in tracking fermentation behavior. Computer control schemes for fermentation can focus on high productivity, high product titer, or minimum cost. Computer systems may perform on-line optimization of fermentation. Progress has been slow by empirical methods because there is a multiplicity of variables and because statistical techniques suffer from the relatively poor reproducibility of fermentations. Careful attention to preparation of inoculum, time/temperature factors of sterilization, and the timing of inoculation and feeding can greatly reduce variability of bioprocess performance.

ENZYME ENGINEERING

ENZYMATIC REACTION KINETICS

Enzymes are excellent catalysts for two reasons: great specificity and high turnover rates. With but few exceptions, all reactions in biological systems are catalyzed by enzymes, and each enzyme usually catalyzes only one reaction. For most of the important enzymes and other proteins, the amino-acid sequences and three-dimensional structures have been determined. When the molecular structure of an enzyme is known, a precise molecular weight could be used to state concentration in molar units. However, the amount is usually expressed in terms of catalytic activity because some of the enzyme may be denatured or otherwise inactive. An international unit (IU) of an enzyme is defined as the amount capable of producing one micromole of its reaction product in one minute under its optimal (or some defined) reaction conditions. Specific activity, the activity per unit mass, is an index of enzyme purity.

Although the mechanisms may be complicated and varied, some simple equations can often describe the reaction kinetics of common enzymatic reactions quite well. Each enzyme molecule is considered to have an active site that must first encounter the substrate (reactant) to form a complex so that the enzyme can function. Accordingly, the following reaction scheme is written:

$$E + S \underset{2}{\overset{1}{\rightleftharpoons}} ES \xrightarrow{3} P + E \tag{24-31}$$

where E = enzyme, S = substrate, ES = enzyme-substrate complex, and P = product.

Reactions 1 and 2 may be assumed to be in equilibrium soon after the enzyme is exposed to its substrate. Rate equations for these reactions are:

$$\frac{d(S)}{dt} = k_2(ES) - k_1(E)(S) \tag{24-32}$$

$$\frac{d(ES)}{dt} = k_1(E)(S) - (k_1 + k_3)(ES) \tag{24-33}$$

$$\frac{d(P)}{dt} = k_3(ES) \tag{24-34}$$

where k_1, k_2, k_3 = kinetic constants shown with the arrows in Eq. (24-31). Analysis leads to the Michaelis-Menten equation:

$$\frac{d(P)}{dt} = \frac{V_{max}(S)}{K_M + (S)} \tag{24-35}$$

where K_M = Michaelis Constant and V_{max} = maximum rate of reaction.

This equation successfully describes the kinetic behavior of a surprisingly large number of reactions of different enzymes. Taking reciprocals of both sides gives:

$$\frac{dt}{d(P)} = \frac{K_M}{(S)\,V_{max}} + \frac{1}{V_{max}} \tag{24-36}$$

A linear plot of the reciprocal of the reaction rate versus $1/(S)$ will allow the determination of K_M and V_{max} from experimental data.

Kinetic behavior becomes complicated when there are two chemical species that can both complex with the enzyme molecules. One of the species might behave as an inhibitor of the enzyme reaction with the other as the substrate. Depending upon the nature of the complex, different inhibition patterns will yield different kinetic equations. For example:

$$E + S \rightleftharpoons ES \rightarrow P + E \tag{24-37}$$

$$E + I \rightleftharpoons EI \tag{24-38}$$

Since the EI complex does not yield product P, and I competes with S for E, there is a state of *competitive inhibition.* By analogy to the Michaelis-Menten equation:

$$\frac{dt}{d[P]} = \frac{K_M}{V_{max}}\frac{1}{S}\left(1 + \frac{[I]}{K_i}\right) + \frac{1}{V_{max}} \tag{24-39}$$

where I = concentration of the competitive inhibitor and K_i = inhibition constant.

Enzyme reactions are also sensitive to pH and temperature changes. In characterizing an enzyme, its optimal pH and optimal temperature are conditions at which the enzyme has its highest catalytic activity.

For a somewhat more extensive exposure to enzyme reaction kinetics, consult standard biochemistry texts and also Dixon, M. and E. C. Webb, *Enzymes,* 2d ed., Academic Press, 1964; Segal, I. H., *Enzyme Kinetics,* Wiley, 1975; Gacesa, P. and J. Hubble, *Enzyme Technology,* Open University Press, England, 1987.

Immobilized Enzymes One factor that usually impedes the development of wide industrial application of enzymes is high cost. Immobilization is a technique to retain enzyme molecules for repeated use. The method of immobilization can be adsorption, covalent bonding, or entrapment. Semipermeable membranes in the form of flat sheets or hollow fibers are one way to restrain the enzyme while allowing smaller molecules to pass. Polyacrylamide gel, silica gel, and other similar materials have been used for entrapment of biologically active materials including enzymes. Encapsulation is another means of capture by coating liquid droplets containing enzymes with some semipermeable materials formed in situ. Generally speaking, entrapment does not involve a chemical or physical/chemical reaction directly with the enzyme molecules; and the enzyme molecules are not altered. Physical adsorption on active carbon particles and ionic adsorption on ion-exchange resins are important for enzyme immobilization. A method with a myriad of possible variations is covalent bonding of the enzyme to a selected carrier. Materials such as glass particles, cellulose, silica, and so on, have been used as carriers for immobilization. Enzymes immobilized by entrapment and adsorption may be subject to loss due to leakage or desorption. On the other hand, the chemical treatment in forming the covalent bond between an enzyme and its carrier may permanently damage some enzyme molecules. In enzyme immobilization, two efficiency terms are often used. Immobilization yield can be used to describe the percent of enzyme activity that is immobilized,

$$\%\ \text{yield} = 100 \times \frac{\text{activity immobilized}}{\text{starting activity}}$$

Immobilization efficiency describes the percent of enzyme activity that is observed:

$$\text{percent efficiency} = 100 \times \frac{\text{observed activity}}{\text{activity immobilized}}$$

When an enzyme molecule is attached to a carrier, its active site might be sterically blocked and thus its activity becomes unobservable (inactivated).

One of the most important parameters of an immobilized-carrier complex is stability of its activity. Catalytic activity of the complex diminishes with time because of leakage, desorption, deactivation, and the like. The half-life of the complex is often used to describe the activity stability. Even though there may be frequent exceptions, linear decay is often assumed in treating the kinetics of activity decay of an immobilized complex.

Immobilization by adsorption or by covalent bonding often helps to stabilize the molecular configurations of an enzyme against alternations including those that may cause thermal deactivation. Immobilized enzymes tend to be less sensitive to pH changes than are free enzymes. Although careful choice of the immobilization chemistry can result in stabilized activity, there are some enzymes that are much less stable after immobilization. Most carriers are designed to have high porosity and large internal surface areas so that a relatively large amount of enzymes can be immobilized onto a given volume or given weight of the carrier. Therefore, in an immobilized enzyme-carrier complex, the enzyme molecules are subject to the effect of the microenvironment in the pores of the complex. Surface charges and other microenvironmental effects can create a shift up or down of optimal pH of the enzyme activity.

An immobilized enzyme-carrier complex is a special case that can employ the methodology developed for evaluation of a heterogeneous catalytic system. The enzyme complex also has external diffusional effects, pore diffusional effects, and an effectiveness factor. When carried out in aqueous solutions, heat transfer is usually good, and it is safe to assume that isothermal conditions prevail for an immobilized enzyme complex.

The Michaelis-Menten equation and other similar nonlinear expressions characterize immobilized enzyme kinetics. Therefore, for a spherical porous carrier particle with enzyme molecules immobilized on its external as well as internal surfaces, material balance of the substrate will result in the following:

$$2\frac{D_e}{r}\frac{dS}{dr} + D_e\frac{d^2S}{dr^2} = \frac{V_{\max}S}{K_M + S} \qquad (24\text{-}40)$$

with also the usual boundary conditions, at $r = R$, $S = S$ and at $r = 0$, $dS/dr = 0$ where R = radius of the sphere, r = distance from sphere center, S = substrate concentration, and D_e = effective diffusivity. Normalizing results in:

$$\frac{d^2y}{dx^2} + \frac{2}{x}\frac{dy}{dx} - \phi^2\beta\left(\frac{y}{\beta} + y\right) = 0 \qquad (24\text{-}41)$$

where y is dimensionless concentration, x is dimensionless distance, and ϕ and β are dimensionless constants; ϕ is sometimes referred to as the Thiele modulus of the immobilized enzyme complex. The boundary conditions are $x = 1$, $y = 1$ and at $x = 0$, $dy/dx = 0$. Graphical solutions are available in standard tests. Two meaningful asymptotic conditions have analytical solutions. In one extreme, $\beta \to 0$, meaning $S >> K_m$, and accordingly the Michaelis-Menten equation reduces to a zero-order reaction with $V = V_{max}$. This is the condition of saturation (i.e., the substrate supply is high and saturates all of the active sites of the enzyme molecules). In the other extreme, $\beta \to \infty$, meaning $K_m >> S$, and accordingly the Michaelis-Menten equation approaches that of a first-order reaction with $V = V_{\max}S/K_m$. This is the condition of a complete substrate control.

Enzymatic Reactors Adding free enzyme to a batch reactor is practical only when the value of the enzyme is relatively low. With expensive enzymes, reuse by retaining the enzyme with some type of support makes great economic sense. As some activity is usually lost in tethering the enzyme and the additional operations cost money, stability is very important. However, many enzymes are stabilized by immobilization; thus, many reuses may be possible.

Methods of immobilization have already been discussed, and various reactor configurations are possible. An enzyme immobilized on beads of a support material or captured in a gel droplet is essentially a catalytic particle. Mounted in a packed column, there may be upflow or downflow of the feed solution, and a fluidized bed may be feasible except that particle collision often endangers stability of the enzyme. A serious problem is growth of microorganisms on the particles because enzymes are proteins that are nutritious. As immobilized enzymes often have more thermal stability than do free enzymes, the columns can be run at elevated temperatures (50 to 65°C, or 122 to 149°F) to improve reaction rate and to inhibit most but not all contaminating organisms. Sterile feed solutions and aseptic technique can minimize contamination, but, more commonly, antiseptics are added to the feed, and there is occasional treatment with a toxic chemical to wash organisms from the column. Particles with immobilized enzymes are sometimes added to a reactor and recovered later by filtration or by some trick such as using magnets to collect enzymes attached to iron.

Cellulose is hydrolyzed by a complex of several enzymes. The mix of enzyme activities produced by mold cultures can have insufficient amounts of the enzyme beta-glucosidase to maintain a commercially acceptable hydrolysis rate. This enzyme can be produced with a different microbial culture and used to supplement the original enzyme mix, but the cost is high. It is logical to immobilize the beta-glucosidase for multiple use. Handling is minimized by circulating fluid from the main reactor through an external packed column of immobilized enzyme.

Enzymes can be immobilized in sheets. One design had discs of enzymes fastened to a rotating shaft to improve mass transfer, and an alternate design had the feed stream flowing back and forth through sandwiches of sheets with enzyme. However, volumetric efficiency of such reactors is low because sheets with finite spacing offer less area than that of packed particles.

It is possible to add free enzyme and recover it by ultrafiltration, but sufficient membrane surface to get good rates and the required auxiliary equipment are expensive. A hollow fiber device packs a vast amount of membrane area into a small volume. Enzyme may be immobilized inside or outside of the fiber, and it is easy to flush and replace the enzyme. Drawbacks to this design are: (1) The stability of the enzyme is not affected—activity that survives the immobilization step can have enhanced long-term stability; (2) there are two mass-transfer steps, as the substrate must diffuse through the fiber to reach the enzyme and the product must diffuse back; and (3) diffusion is poor on the outside of packed fibers. There is a scheme with the enzyme immobilized on or in the membrane to provide excellent contact as the feed is forced through. Although not yet commercialized, this method appears quite attractive. Recent Russian research with quick freezing has produced gels of enzymes that have high activity, good stability, and a temperature range up to the point where the gel collapses.

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Section 25

Waste Management

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List of Abbreviations

Abbreviation	Definition
3P	Pollution prevention pays
ABS	Alkyl benzene sulfonate
ACC	Annualized capital costs
BACT	Best available control technology
BAT	Best available technology
BCOD	Biodegradable chemical oxygen demand
BCT	Best conventional technology
BOD	Biochemical oxygen demand
BSRT	Biomass solids retention time
BTEX	Benzene, toluene, xylene
CAA	Clean Air Act
CAAA	Clean Air Act Amended
CCP	Comprehensive costing procedures
CFR	Code of federal regulations
COD	Chemical oxygen demand
CPI	Chemical process industries
CRF	Capital recovery factor
CTDMPLUS	Complex terrain dispersion model plus algorithms for unstable situations
CWRT	Center for Waste Reduction Technologies
DCF	Direct installation cost factor
DO	Dissolved oxygen
DRE	Destruction and removal efficiency
EBCT	Empty bed contact time
EPA	Environmental Protection Agency
FML	Flexible membrane liner
GAX	Granular activated carbon
HAPS	Hazardous air pollutants
HAZWOPER	Hazardous waste operators
HCS	Hauled-container systems
HRT	Reactor hydraulic retention time
HSWA	Hazardous and Solid Waste Act
I-TEF	International toxic equivalency factor
ICF	Indirect installation cost factor
ISO	International Organization for Standardization
LCA	Life cycle assessment
LCC	Life cycle costing
LOX	Liquid oxygen

Abbreviation	Definition
MACT	Maximum achievable control technology
MSDA	Material safety data sheets
MSW	Municipal solid waste
MWC	Municipal waste combustors
MWI	Medical waste incinerators
NBOD	Nitrogenous biochemical oxygen demand
NIMBY	Not in my back yard
NPDES	National pollutant discharge elimination system
NSPS	New source performance standards
PCB	Polychlorinated biphenyl
PIES	Pollution prevention information exchange systems
PM	Particulate matter
POTW	Publicly owned treatment work
PPIC	Pollution prevention information clearinghouse
PSD	Prevention of significant deterioration
RCRA	Resource Conservation and Recovery Act
RDF	Refuse-derived fuel
SARA	Superfund Amendments and Reauthorization Act
SCR	Selective catalytic reduction
SCS	Stationary-container systems
SE	Strength of the treated waste
SMART	Save money and reduce toxics
SO	Strength of the untreated waste
SS	Suspended solids
TCC	Total capital cost
TCP	Traditional costing procedures
TGNMO	Total gas nonmethane organics
TOC	Total organic carbon
TSA	Total systems approach
TSCA	Toxic Substances Control Act
TSD	Treatment, storage, and disposal
UASB	Upflow anerobic sludge blanket
VOC	Volatile organic compound
VOST	Volatile organic sampling train
VSS	Volatile suspended solids
WRAP	Waste reduction always pays
WTE	Waste-to-energy (systems)

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INTRODUCTION TO WASTE MANAGEMENT

In this section, a number of references are made to laws and procedures that have been formulated in the United States with respect to waste management. An engineer handling waste-management problems in another country would well be advised to know the specific laws and regulations of that country. Nevertheless, the treatment given here is believed to be useful as a general guide.

Multimedia Approach to Environmental Regulations in the United States Among the most complex problems to be faced by industry during the 1990s is the proper control and use of the natural environment. In the 1970s the engineering profession became acutely aware of its responsibility to society, particularly for the protection of public health and welfare. The decade saw the formation and rapid growth of the U.S. Environmental Protection Agency (EPA) and the passage of federal and state laws governing virtually every aspect of the environment. The end of the decade, however, brought a realization that only the more simplistic problems had been addressed. A limited number of large sources had removed substantial percentages of a few readily definable air pollutants from their emissions. The incremental costs to improve the removal percentages would be significant and would involve increasing numbers of smaller sources, and the health hazards of a host of additional toxic pollutants remained to be quantified and control techniques developed.

Moreover, in the 1970s, air, water, and waste were treated as separate problem areas to be governed by their own statutes and regulations. Toward the latter part of the decade, however, it became obvious that environmental problems were closely interwoven and should be treated in concert. The traditional type of regulation—command and control—had severely restricted compliance options.

The 1980s began with EPA efforts redirected to take advantage of the case-specific knowledge, technical expertise, and imagination of those being regulated. Providing plant engineers with an incentive to find more efficient ways of abating pollution would greatly stimulate innovation in control technology. This is a principal objective, for example, of EPA's "controlled trading" air pollution program, established in the Offsets Policy Interpretative Ruling issued by the EPA in 1976, with statutory foundation given by the Clean Air Act Amendments of 1977. The Clean Air Act Amendments of 1990 expanded the program even more to the control of sulfur oxides under Title IV. In effect, a commodities market on "clean air" was developed.

The rapidly expanding body of federal regulation presents an awesome challenge to traditional practices of corporate decision-making, management, and long-range planning. Those responsible for new plants must take stock of the emerging requirements and construct a fresh approach.

The full impact of the Clean Air Act Amendments of 1990, the Clean Water Act, the Safe Drinking Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Responsibility, Compensation and Liability (Superfund) Act, and the Toxic Substances Control Act is still not generally appreciated. The combination of all these requirements, sometimes imposing conflicting demands or establishing differing time schedules, makes the task of obtaining all regulatory approvals extremely complex.

One of the dominant impacts of environmental regulations is that the lead time required for the planning and construction of new plants is substantially increased. When new plants generate major environmental complexities, the implications can be profound. Of course, the exact extent of additions to lead time will vary widely from one case to another, depending on which permit requirements apply and on what difficulties are encountered. For major expansions in any field of heavy industry, however, the delay resulting from federal requirements could conceivably add 2 to 3 years to total lead time. Moreover, there is always the possibility that regulatory approval will be denied. So, contingency plans for fulfilling production needs must be developed.

Any company planning a major expansion must concentrate on environmental factors from the outset. Since many environmental approvals require a public hearing, the views of local elected officials and the com-

munity at large are extremely important. To an unprecedented degree, the political acceptability of a project can now be crucial.

Plant Strategies At the plant level, a number of things can be done to minimize the impact of environmental quality requirements. These include:

1. Maintaining an accurate source-emission inventory
2. Continually evaluating process operations to identify potential modifications that might reduce or eliminate environmental impacts
3. Ensuring that good housekeeping and strong preventive-maintenance programs exist and are followed
4. Investigating available and emerging pollution-control technologies
5. Keeping well informed of the regulations and the directions in which they are moving
6. Working closely with the appropriate regulatory agencies and maintaining open communications to discuss the effects that new regulations may have
7. Keeping the public informed through a good public-relations program.

It is unrealistic to expect that at any point in the foreseeable future Congress will reverse direction, reduce the effect of regulatory controls, or reestablish the preexisting legal situation in which private companies are free to construct major industrial facilities with little or no restraint by federal regulation.

Corporate Strategic Planning Contingency planning represents an essential component of sound environmental planning for a new plant. The environmental uncertainties surrounding a large capital project should be specified and related to other contingencies (such as marketing, competitive reactions, politics, foreign trade, etc.) and mapped out in the overall corporate strategy.

Environmental factors should also be incorporated into a company's technical or research and development program. Since the planning horizons for new projects may now extend to 5 to 10 years, R&D programs can be designed for specific projects. These may include new process modifications or end-of-pipe control technologies.

Another clear need is to integrate environmental factors into financial planning for major projects. It must be recognized that strategic environmental planning is as important to the long-range goal of the corporation as is financial planning. Trade-off decisions regarding financing may have to change as the project goes through successive stages of environmental planning and permit negotiations. For example, requirements for the use of more expensive pollution control technology may significantly increase total project costs; or a change from end-of-pipe to process modification technology may preclude the use of industrial revenue bond financing under Internal Revenue Service (IRS) rules. Regulatory delays can affect assumptions as to both the rate of expenditure and inflation factors. Investment, production, environmental, and legal factors are all interrelated and can have a major impact on corporate cash flow.

Most companies must learn to deal more creatively with local officials and public opinion. The social responsibility of companies can become an extremely important issue. Companies should apply thoughtfulness and skill to the timing and conduct of public hearings. Management must recognize that local officials have views and constituencies that go beyond attracting new jobs.

From all these factors, it is clear that the approval and construction of major new industrial plants or expansions is a far more complicated operation than it has been in the past, even the recent past. Stringent environmental restrictions are likely to preclude construction of certain facilities at locations where they otherwise might have been built. In other cases, acquisition of required approvals may generate a heated technical and political debate that can drag out the regulatory process for several years.

In many instances, new requirements may be imposed while a company is seeking approval for a proposed new plant. Thus, companies intending to expand their basic production facilities should anticipate their needs far in advance, begin preparation to meet the regulatory challenge they will eventually confront, and select sites with careful consideration of environmental attributes. It is the objective of this section to assist the engineer in meeting this environmental regulatory challenge.

UNITED STATES AIR QUALITY LEGISLATION AND REGULATIONS

Although considerable federal legislation dealing with air pollution has been enacted since the 1950s, the basic statutory framework now in effect was established by the Clean Air Act of 1970; amended in 1974 to deal with energy-related issues; amended in 1977, when a number of amendments containing particularly important provisions associated with the approval of new industrial plants were adopted; and amended in 1990 to address toxic air pollutants and ozone nonattainment areas.

Clean Air Act of 1970 The Clean Air Act of 1970 was founded on the concept of attaining National Ambient Air Quality Standards (NAAQS). Data were accumulated and analyzed to establish the quality of the air, identify sources of pollution, determine how pollutants disperse and interact in the ambient air, and define reductions and controls necessary to achieve air-quality objectives.

EPA promulgated the basic set of current ambient air-quality standards in April 1971. The specific regulated pollutants were particulates, sulfur dioxide, photochemical oxidants, hydrocarbons, carbon monoxide, and nitrogen oxides. In 1978, lead was added. Table 25-1 enumerates the present standards.

To provide basic geographic units for the air-pollution control program, the United States was divided into 247 air quality control regions (AQCRs). By a standard rollback approach, the total quantity of pollution in a region was estimated, the quantity of pollution that could be tolerated without exceeding standards was then calculated, and the degree of reduction called for was determined. States were required by EPA to develop state implementation plans (SIPs) to achieve compliance.

The act also directed EPA to set new source performance standards (NSPS) for specific industrial categories. New plants were required to use the best system of emission reduction available. EPA gradually issued these standards, which now cover a number of basic industrial categories (as listed in Table 25-2). The 1977 amendments to the Clean Air Act directed EPA to accelerate the NSPS program and included a regulatory program to prevent significant deterioration in those areas of the country where the NAAQS were being attained.

Finally, Sec. 112 of the Clean Air Act required that EPA promulgate National Emission Standards for Hazardous Air Pollutants (NESHAPs). Between 1970 and 1989, standards were promulgated for asbestos, beryllium, mercury, vinyl chloride, benzene, arsenic, radionuclides, and coke-oven emissions.

Prevention of Significant Deterioration (PSD) Of all the federal laws placing environmental controls on industry (and, in particular, on new plants), perhaps the most confusing and restrictive are the limits imposed for the prevention of significant deterioration (PSD) of air quality. These limits apply to areas of the country that are already cleaner than required by ambient air-quality standards. This regulatory framework evolved from judicial and administrative action under the 1970 Clean Air Act and subsequently was given full statutory foundation by the 1977 Clean Air Act Amendments.

EPA established an area classification scheme to be applied in all such regions. The basic idea was to allow a moderate amount of industrial development but not enough to degrade air quality to a point at which it barely complied with standards. In addition, states were to designate certain areas where pristine air quality was especially desirable. All air-quality areas were categorized as Class I, Class II, or Class III. Class I areas were pristine areas subject to the tightest control. Permanently designated Class I areas included international parks, national wilderness areas, memorial parks exceeding 5000 acres, and national parks exceeding 6000 acres. Although the nature of these areas is such that industrial projects would not be located within them, their Class I status could affect projects in neighboring areas where meteorological conditions might result in the transport of emissions into them. Class II areas were areas of moderate industrial growth. Class III areas were areas of major industrialization. Under EPA regulations promulgated in December 1974, all areas were initially categorized as Class II. States were authorized to reclassify specified areas as Class I or Class III.

The EPA regulations also established another critical concept

TABLE 25-1 National Primary and Secondary Ambient Air Quality Standards

Pollutant	Averaging time	Primary standards	Secondary standards
Sulfur oxides	Annual arithmetic mean	80 μg/m^3 (0.03 ppm)	
	24 h	365 μg/m^3 (0.14 ppm)	
	3 h		1,300 μg/m^3 (0.5 ppm)
Particulate matter	Annual geometric mean	75 μg/m^3	60 μg/m^3
(PM_{10}, particulates with aerodynamic diameter less than or equal to 10 microns)	24 h	260 μg/m^3	150 μg/m^3
Ozone	1 h	240 μg/m^3 (0.12 ppm)	Same as primary standard
Carbon monoxide	8 h	10 mg/m^3	Same as primary standard
	1 h	40 mg/m^3 (35 ppm)	
Nitrogen oxides	Annual arithmetic mean	100 μg/m^3 (0.05 ppm)	Same as primary standard
Lead	3 months	1.5 μg/m^3	Same as primary standard

NOTE: National standards, other than those based on annual arithmetic means or annual geometric means, are not to be exceeded more than once a year.

TABLE 25-2 Source Categories for Which New Source Performance Standards Have Been Set as of 1991

- Fossil-Fuel-Fired Steam Generators for Which Construction Commenced after August 17, 1971
- Electric Utility Steam Generating Units for Which Construction Commenced after September 18, 1978
- Industrial-Commercial-Institutional Steam Generating Units
- Incinerators
- Portland Cement Plants
- Nitric Acid Plants
- Sulfuric Acid Plants
- Asphalt Concrete Plants
- Petroleum Refineries
- Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced after June 11, 1973, and Prior to May 19, 1978
- Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced after May 18, 1978, and Prior to July 23, 1984
- Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced after July 23, 1984
- Secondary Lead Smelters
- Secondary Brass and Bronze Production Plants
- Primary Emissions from Basic Oxygen Process Furnaces for Which Construction Commenced after June 11, 1973
- Secondary Emissions from Basic Oxygen Process Steelmaking Facilities for Which Construction Commenced after January 20, 1983
- Sewage Treatment Plants
- Primary Copper Smelters
- Primary Zinc Smelters
- Primary Lead Smelters
- Primary Aluminum Reduction Plants
- Phosphate Fertilizer Industry: Wet-Process Phosphoric Acid Plants
- Phosphate Fertilizer Industry: Superphosphoric Acid Plants
- Phosphate Fertilizer Industry: Diammonium Phosphate Plants
- Phosphate Fertilizer Industry: Triple Superphosphate Plants
- Phosphate Fertilizer Industry: Granular Triple Superphosphate Storage Facilities
- Coal Preparation Plants
- Ferroalloy Production Facilities
- Steel Plants: Electric Arc Furnaces Constructed after October 21, 1974, and on or before August 17, 1983
- Steel Plants: Electric Arc Furnaces and Argon-Oxygen Decarburization Vessels Constructed after August 7, 1983
- Kraft Pulp Mills
- Glass Manufacturing Plants
- Grain Elevators
- Surface Coating of Metal Furniture
- Stationary Gas Turbines
- Lime Manufacturing Plants
- Lead-Acid Battery Manufacturing Plants
- Metallic Mineral Processing Plants
- Automobile and Light-Duty Truck Surface Coating Operations
- Phosphate Rock Plants
- Ammonium Sulfate Manufacture
- Graphic Arts Industry: Publication Rotogravure Printing
- Pressure-Sensitive Tape and Label Surface Coating Operations
- Metal Coil Surface Coating
- Asphalt Processing and Asphalt Roofing Manufacture
- Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry
- Beverage Can Surface Coating Industry
- Bulk Gasoline Terminals
- New Residential Wood Heaters
- Rubber Tire Manufacturing Industry
- Flexible Vinyl and Urethane Coating and Printing
- Equipment Leaks of VOC in Petroleum Refineries
- Synthetic Fiber Production Facilities
- Petroleum Dry Cleaners
- Equipment Leaks of VOC from Onshore Natural Gas Processing Plants
- Onshore Natural Gas Processing; SO_2 Emissions
- Nonmetallic Mineral Processing Plants
- Wool Fiberglass Insulation Manufacturing Plants
- VOC Emissions from Petroleum Refinery Wastewater Systems
- Magnetic Tape Coating Facilities
- Industrial Surface Coating: Surface Coating of Plastic Parts for Business Machines
- Volatile Organic Compound Emissions from Synthetic Organic Chemical Manufacturing Industry (SOCMI) Air Oxidation Unit Processes
- Volatile Organic Compound Emissions from Synthetic Organic Chemical Manufacturing Industry Distillation Operations
- Polymeric Coating of Supporting Substrates Facilities

known as the *increment*. This was the numerical definition of the amount of additional pollution that may be allowed through the combined effects of all new growth in a particular locality (see Table 25-3). To assure that the increments would not be used up hastily, EPA specified that each major new plant must install best available control technology (BACT) to limit emissions. This reinforced the same policy underlying the NSPS; and where an NSPS had been promulgated, it would control determinations of BACT. Where such standards had not been promulgated, an ad hoc determination was called for in each case.

To implement these controls, EPA requires that every new source undergo preconstruction review. The regulations prohibited a company from commencing construction on a new source until the review had been completed and provided that, as part of the review procedure, public notice should be given and an opportunity provided for a public hearing on any disputed questions.

Sources Subject to Prevention of Significant Deterioration (PSD) Sources subject to PSD regulations (40 CFR, Sec. 52.21, Aug. 7, 1980) are major stationary sources and major modifications located in attainment areas and unclassified areas. A major stationary source was defined as any source listed in Table 25-4 with the potential to emit 100 tons per year or more of any pollutant regulated under the Clean Air Act (CAA) or any other source with the potential to emit 250 tons per year or more of any CAA pollutant. The "potential to emit" is defined as the maximum capacity to emit the pollutant under applicable emission standards and permit conditions (after application of any air pollution control equipment) excluding secondary emissions. A "major modification" is defined as any physical or operational change of a major stationary source producing a "significant net emissions increase" of any CAA pollutant (see Table 25-5).

Ambient monitoring is required of all CAA pollutants with emissions greater than or equal to Table 25-5 values for which there are

TABLE 25-3 Prevention of Significant Deterioration (PSD) Air-Quality Increments

	Maximum allowable increase over baseline air quality, μg/m³			Primary ambient air-quality standard, μg/m³
	Class I	Class II	Class III	
Particulate matter				
Annual geometric mean	5	19	37	75
24-h maximum	10	37	75	260
SO_2				
Annual arithmetic mean	2	20	40	80
24-h maximum	5	91	182	365
3-h maximum	25	512	700	1300*

*Secondary standard rather than primary standard.

TABLE 25-4 Sources Subject to PSD Regulation if Their Potential to Emit Equals or Exceeds 100 Tons per Year

Fossil-fuel-fired steam electric plants of more than 250 million Btu/h heat input
Coal-cleaning plants (with thermal dryers)
Kraft-pulp mills
Portland-cement plants
Primary zinc smelters
Iron and steel mill plants
Primary aluminum-ore-reduction plants
Primary copper smelters
Municipal incinerators capable of charging more than 250 tons of refuse per day
Hydrofluoric, sulfuric, and nitric acid plants
Petroleum refineries
Lime plants
Phosphate-rock-processing plants
Coke-oven batteries
Sulfur-recovery plants
Carbon-black plants (furnace process)
Primary lead smelters
Fuel-conversion plants
Sintering plants
Secondary metal-production plants
Chemical-process plants
Fossil-fuel boilers (or combinations thereof) totaling more than 250 million Btu/h heat input
Petroleum-storage and -transfer units with total storage capacity exceeding 300,000 bbl
Taconite-ore-processing plants
Glass-fiber-processing plants
Charcoal-production plants

TABLE 25-5 Significant Net Emissions Increase

Pollutant	Tons/year
CO	100
NO_x (as NO_2)	40
SO_2	40
Particulate matter	25
Ozone	40 of volatile organic compounds
Lead	0.6
Asbestos	0.007
Beryllium	0.0004
Mercury	0.1
Vinyl chloride	1
Fluorides	3
Sulfuric acid mist	7
Hydrogen sulfide	10
Total reduced sulfur	10
Reduced-sulfur compounds	10
Other CAA pollutants	>0

NAAQS. Continuous monitoring is also required for other CAA pollutants for which the EPA or the state determines that monitoring is necessary. The EPA or the state may exempt any CAA pollutant from these monitoring requirements if the maximum air-quality impact of the emissions increase is less than the values in Table 25-6 or if present concentrations of the pollutant in the area that the new source would affect are less than the Table 25-6 values. The EPA or the state may accept representative existing monitoring data collected within 3 years of the permit application to satisfy monitoring requirements.

EPA regulations provide exemption from BACT and ambient air-impact analysis if the modification that would increase emissions is accompanied by other changes within the plant that would net a zero increase in total emissions. This exemption is referred to as the "bubble" or "no net increase" exemption.

A full PSD review would include a case-by-case determination of the controls required by BACT, an ambient air-impact analysis to determine whether the source might violate applicable increments or air-quality standards; an assessment of the effect on visibility, soils, and vegetation; submission of monitoring data; and full public review.

EPA regulations exempted smaller sources from the major elements of PSD review and, in particular, relieved those sources from compliance with BACT (though they still had to comply with applicable NSPS as well as with requirements under the SIP program). Smaller sources were also exempted from conducting ambient air-impact analysis and submitting data supporting an ambient air-quality analysis. Smaller sources, however, were not exempted from the program altogether. They remained subject to the statutory requirements to obtain preconstruction approval, including procedures for public review, and they still might be required, at EPA request, to submit data supporting their applications. Also, if emissions from a smaller source would affect a Class I area or if an applicable increment were already being violated, the full PSD requirements for ambient air-impact analysis would apply.

Nonattainment (NA) Those areas of the United States failing to attain compliance with ambient air-quality standards were considered nonattainment areas. New plants could be constructed in nonattainment areas only if stringent conditions were met. Emissions had to be controlled to the greatest degree possible, and more than equivalent offsetting emission reductions had to be obtained from other sources to assure progress toward achievement of the ambient air-quality standards. Specifically, (1) the new source must be equipped with pollution controls to assure lowest achievable emission rate (LAER), which in no case can be less stringent than any applicable NSPS; (2) all existing sources owned by an applicant in the same region must be in compliance with applicable state implementation plan requirements or be under an approved schedule or an enforcement order to achieve such compliance; (3) the applicant must have sufficient offsets to more than

TABLE 25-6 Concentration Impacts below Which Ambient Monitoring May Not Be Required

	μg/m³	Average time
CO	575	8-h maximum
NO_2	14	24-h maximum
TSP	10	24-h maximum
SO_2	13	24-h maximum
Lead	0.1	24-h maximum
Mercury	0.25	24-h maximum
Beryllium	0.0005	24-h maximum
Fluorides	0.25	24-h maximum
Vinyl chloride	15	24-h maximum
Total reduced sulfur	10	1-h maximum
H_2S	0.04	1-h maximum
Reduced-sulfur compounds	10	1-h maximum

make up for the emissions to be generated by the new source (after application of LAER); and (4) the emission offsets must provide "a positive net air quality benefit in the affected area."

LAER was deliberately a technology-forcing standard of control. The statute stated that LAER must reflect (1) the most stringent emission limitation contained in the implementation plan of any state for such category of sources unless the applicant can demonstrate that such a limitation is not achievable, or (2) the most stringent limitation achievable in practice within the industrial category, whichever is more stringent. In no event could LAER be less stringent than any applicable NSPS. While the statutory language defining BACT directed that "energy, environmental, and economic impacts and other costs" be taken into account, the comparable provision on LAER provided no instruction that economics be considered.

For existing sources emitting pollutants for which the area is nonattainment, reasonable available control technology (RACT) would be required. EPA defines RACT by industrial category.

Controlled-Trading Program The legislation enacted under the Clean Air Act Amendments of 1977 provided the foundation for EPA's controlled-trading program, the essential elements of which include:

- Bubble policy (or bubble exemption under PSD)
- Offsets policy (under nonattainment)
- Banking and brokerage (under nonattainment)

While these different policies vary broadly in form, their objective is essentially the same: to substitute flexible economic-incentive systems for the current rigid, technology-based regulations that specify exactly how companies must comply. These market mechanisms have made regulating easier for EPA and less burdensome and costly for industry.

Bubble Policy The bubble concept introduced under PSD provisions of the Clean Air Act Amendments of 1977 was formally proposed as EPA policy on Jan. 18, 1979, the final policy statement being issued on Dec. 11, 1979. The bubble policy allows a company to find the most efficient way to control a plant's emissions as a whole rather than by meeting individual point-source requirements. If it is found less expensive to tighten control of a pollutant at one point and relax controls at another, this would be possible as long as the total pollution from the plant would not exceed the sum of the current limits on individual point sources of pollution in the plant. Properly applied, this approach would promote greater economic efficiency and increased technological innovation.

There are some restrictions, however, in applying the bubble concept:

1. The bubble may be only used for pollutants in an area where the state implementation plan has an approved schedule to meet air-quality standards for that pollutant.
2. The alternatives used must ensure that air-quality standards will be met.
3. Emissions must be quantifiable, and trades among them must be even. Each emission point must have a specific emission limit, and that limit must be tied to enforceable testing techniques.
4. Only pollutants of the same type may be traded; that is, particulates for particulates, hydrocarbons for hydrocarbons, etc.
5. Control of hazardous pollutants cannot be relaxed through trades with less toxic pollutants.
6. Development of the bubble plan cannot delay enforcement of federal and state requirements.

Some additional considerations must be noted:

1. The bubble may cover more than one plant within the same area.
2. In some circumstances, states may consider trading open dust emissions for particulates (although EPA warns that this type of trading will be difficult).
3. EPA may approve compliance date extensions in special cases. For example, a source may obtain a delay in a compliance schedule to install a scrubber if such a delay would have been permissible without the bubble.

EPA will closely examine particulate size distribution in particulate emission trades because finer particulates disperse more widely, remain in the air longer, and frequently are associated with more adverse health effects.

It will be the responsibility of industry to suggest alternative control approaches and demonstrate satisfactorily that the proposal is equivalent in pollution reduction, enforceability, and environmental impact to existing individual process standards.

Offsets Policy Offsets were EPA's first application of the concept that one source could meet its environmental protection obligations by getting another source to assume additional control actions. In nonattainment areas, pollution from a proposed new source, even one that controls its emissions to the lowest possible level, would aggravate existing violations of ambient air-quality standards and trigger the statutory prohibition. The offsets policy provided these new sources with an alternative. The source could proceed with construction plans, provided that:

1. The source would control emissions to the lowest achievable level.
2. Other sources owned by the applicant were in compliance or on an approved compliance schedule.
3. Existing sources were persuaded to reduce emissions by an amount at least equal to the pollution that the new source would add.

Banking and Brokerage Policy EPA's banking policy is aimed at providing companies with incentives to find more offsets. Under the original offset policy, a firm shutting down or modifying a facility could apply the reduction in emissions to new construction elsewhere in the region only if the changes were made simultaneously. However, with banking a company can "deposit" the reduction for later use or sale. Such a policy will clearly establish that clean air (or the right to use it) has direct economic value.

Clean Air Act of 1990 In November, 1990, Congress adopted the Clean Air Act Amendments of 1990, providing substantial changes to many aspects of the existing CAAA. The concepts of NAAQS, NSPS, and PSD remain virtually unchanged. However, significant changes have occurred in several areas that directly affect industrial facilities and electric utilities and air-pollution control at these facilities. These include changes and additions in the following major areas:

Title I	Nonattainment areas
Title III	Hazardous air pollutants
Title IV	Acid deposition control
Title V	Operating permits

Title I: Nonattainment Areas The existing regulations for nonattainment areas have been made more stringent in several areas. The CAAA of 1990 requires the development of comprehensive emission inventory-tracking for all nonattainment areas and establishes a classification scheme that defines nonattainment areas into levels of severity. For example, ozone nonattainment areas are designated as marginal, moderate, serious, severe (two levels), and extreme, with compliance deadlines of 3, 6, 9, 15–17, and 20 years, respectively, with each classification having more stringent requirements regarding strategies for compliance (see Table 25-7). Volatile organic compound (VOC) emissions reductions of 15 percent are required in moderate areas by 1996 and 3 percent a year thereafter for severe or extreme areas until compliance is achieved. In addition, the definition of a major source of ozone precursors (previously 100 tons per year of NO_x, CO, or VOC emissions) was redefined to as little as 10 tons per year in the extreme classification, with increased offset requirements of 1.5 to 1 for new and modified sources. These requirements place major constraints on affected industries in these nonattainment areas. A similar approach is being taken in PM_{10} and CO nonattainment areas.

Title III: Hazardous Air Pollutants The Title III provisions on hazardous air pollutants (HAPs) represent a major departure from the previous approach of developing NESHAPs. While only eight HAPs were designated in the 20 years since enactment of the CAAA of 1970, the new CAAA of 1990 designated 189 pollutants as HAPs requiring regulation. These are summarized in Table VIII and will affect over 300 major source categories. Major sources are defined as any source (new or existing) that emits (after control) 10 tons a year or more of any regulated HAP or 25 tons a year or more of any combination of HAPs. The deadlines for promulgation of the source categories and appropriate emission standards are as follows:

First 40 source categories	November 15, 1992
Coke oven batteries	December 31, 1992
25% of all listed categories	November 15, 1994

TABLE 25-7 Ozone Nonattainment Area Classifications and Associated Requirements

Nonattainment area classification	One-hour ozone concentration design value, ppm	Attainment date	Major source threshold level, tons VOCs/yr	Offset ratio for new/modified sources
Marginal	0.121–0.138	Nov. 15, 1993	100	1.1 to 1
Moderate	0.138–0.160	Nov. 15, 1996	100	1.15 to 1
Serious	0.160–0.180	Nov. 15, 1999	50	1.2 to 1
Severe	0.180–0.190	Nov. 15, 2005	25	1.3 to 1
	0.190–0.280	Nov. 15, 2007	25	1.3 to 1
Extreme	0.280 and up	Nov. 15, 2010	10	1.5 to 1

Publicly owned treatment works	November 15, 1995
50% of all listed categories	November 15, 1997
100% of all categories	November 15, 2000

Each source will be required to meet maximum achievement control technology (MACT) requirements. For existing sources, MACT is defined as a stringency equivalent to the average of the best 12 percent of the sources in the category. For new sources, MACT is defined as the best controlled system. New sources are required to meet MACT immediately, while existing sources have three years from the date of promulgation of the appropriate MACT standard. As an early incentive, existing sources that undergo at least a 90 percent reduction in emissions of a HAP (or 95 percent for a hazardous particulate) prior to the promulgation of the MACT standard will be issued a six-year extension on the deadline for final compliance.

Title IV: Acid Deposition Control The Acid Deposition Control Program is designed to reduce emissions of SO_2 in the United States by 10 million tons per year, resulting in a net yearly emission of 8.9 million tons by the year 2000. Phase I of the program requires 111 existing uncontrolled coal-fired power plants (≥100 MW) to reduce emissions to 2.5 pounds of SO_2 per 10^6 Btu by 1995 (1997 if scrubbers are used to reduce emissions by at least 90 percent). The reduction is to be accomplished by issuing all affected units emission "allowances" equivalent to what their annual average SO_2 emissions would have been in the years 1985–1987 based on 2.5 pounds SO_2 per 10^6 Btu coal. The regulations represent a significant departure from previous regulations where specified SO_2 removal efficiencies were mandated; rather, the utilities will be allowed the flexibility of choosing which strategies will be used (e.g., coal washing, low-sulfur coal, flue gas desulfurization, etc.) and which units will be controlled, as long as the overall "allowances" are not exceeded. Any excess reduction in SO_2 by a utility will create "banked" emissions that can be sold or used at another unit.

Phase II of Title IV limits the majority of plants ≥20 MW and all plants ≥75 MW to maximum emissions of 1.2 pounds of SO_2 per 10^6 Btu after the year 2000. In general, new plants would have to acquire banked emission allowances in order to be built. Emission allowances will be traded through a combination of sell/purchase with other utilities, EPA auctions and direct sales.

Control of NO_x under the CAAA of 1990 will be accomplished through the issuance of a revised NSPS in 1994, with the objective of reducing emissions by 2 million tons a year from 1980 emission levels. The technology being considered is the use of low-NO_x burners (LNBs). The new emission standards will not apply to cyclone and wet bottom boilers, unless alternative technologies are found, as these cannot be retrofitted with existing LNB technologies.

Title V: Operating Permits Title V of the 1990 Clean Air Act Amendments established a new operating permit program to be administered by state agencies in accordance with federal guidelines. An approved state program will basically require a source to obtain a permit that covers each and every requirement applicable to the source under the Clean Air Act. A major impact of the Title V program is that sources are required to implement measures to demonstrate routinely that they are operating in compliance with permit terms. This represents a dramatic shift from previous practices where, to bring an enforcement action, regulatory authorities were required to demonstrate that a source was in noncompliance.

Initially, all "major" sources of air pollution are required to obtain an operating permit. However, any state permitting authority may extend the applicability of the operating permit to minor sources as well. Once a source is subject to the permit program as a major source for any one pollutant, emissions of every regulated air pollutant must be addressed in the permit application.

The operating permit must outline specifically how and when a source will be allowed to operate over the five-year term of the permit. The permit the state develops from an application becomes the principal mechanism for enforcement of all air-quality regulations. As such, it is critically important to submit an application that allows maximum operating flexibility.

Sources must also include in their permit applications monitoring protocols sufficient to document compliance with each permit term and condition.

The Title V operating permit requires the submission of at least five types of reports:

1. The initial compliance report
2. The annual compliance certification
3. Monitoring reports submitted at least every six months
4. Progress reports for sources not in compliance when the application is submitted
5. Prompt reports on any deviations from the permit terms

Permit fees are a mandatory element of the Title V program. In most cases, fees will be assessed for emissions on a dollars-per-ton-emitted basis.

Regulatory Direction The current direction of regulations and air-pollution control efforts is clearly toward significantly reducing the emissions to the environment of a broad range of compounds, including:

1. Volatile organic compounds and other ozone precursors (CO and NO_x)
2. Hazardous air pollutants, including carcinogenic organic emissions and heavy metal emissions
3. Acid rain precursors, including SO_x and NO_x

In addition, the PM_{10} NAAQS will continue to place emphasis on quantifying and reducing particulate emissions in the less than 10-μm particle-size range. Particle size-specific emission factors have been developed for many sources, and size-specific emission standards have been developed in a number of states. These standards are addressing concerns related to HAP emissions of heavy metals, which are generally associated with the submicron particles.

Although it is not possible to predict the future, it is possible to prepare for it and influence it. It is highly recommended that maximum flexibility be designed into new air-pollution control systems to allow for increasingly more stringent emission standards for both particulates and gases. Further, it is everyone's responsibility to provide a thorough review of existing and proposed new processes and to make every attempt to identify economical process modifications and/or material substitutions that reduce or, in some cases, eliminate both the emissions to the environment and the overdependency on retrofitted or new end-of-pipe control systems.

UNITED STATES WATER QUALITY LEGISLATION AND REGULATIONS

Federal Water Pollution Control Act In 1948, the original Federal Water Pollution Control Act (FWPCA) was passed. This act and its various amendments are often referred to as the Clean Water Act (CWA). It provided loans for treatment plant construction and temporary authority for federal control of interstate water pollution. The enforcement powers were so heavily dependent on the states as

to make the act almost unworkable. In 1956, several amendments to the FWPCA were passed that made federal enforcement procedures less cumbersome. The provision for state consent was removed by amendments passed in 1961, which also extended federal authority to include navigable waters in the United States.

In 1965 the Water Quality Act established a new trend in water pollution control. It provided that the states set water quality standards in accordance with federal guidelines. If the states failed to do so, the standards would be set by the federal government subject to a review hearing. In 1966, the Clean Water Restoration Act transferred the Federal Water Pollution Control Administration from the Department of Health, Education and Welfare to the Department of the Interior. It also gave the Interior Department the responsibility for the Oil Pollution Act.

After the creation of EPA in 1970, the EPA was given the responsibility previously held by the Department of the Interior with respect to water pollution control. In subsequent amendments to the FWPCA in 1973, 1974, 1975, 1976, and 1977, additional Federal programs were established. The goals of these programs were to make waterways of the United States fishable and swimmable by 1983 and to achieve zero discharge of pollutants by 1985. The National Pollutant Discharge Elimination System (NPDES) was established as the basic regulatory mechanism for water pollution control. Under this program, the states were given the authority to issue permits to "point-source" dischargers provided the dischargers gave assurance that the following standards would be met:

1. Source-specific effluent limitations (including New Source Performance Standards)
2. Toxic pollutant regulations (for specific substances regardless of source)
3. Regulations applicable to oil and hazardous substance liability

In order to achieve that stated water-quality goal of fishable and swimmable waters by 1983, each state was required by EPA to adopt water-quality standards that met or exceeded the Federal water quality criteria. After each state submitted its own water-quality standards, which were subsequently approved by EPA, the Federal criteria were removed from the Code of Federal Regulations. The state water-quality standards are used as the basis for establishing both point-source-based effluent limitations and toxic pollutant limitations used in issuing NPDES permits to point-source discharges.

Source-Based Effluent Limitations Under the FWPCA, EPA was responsible for establishing point-source effluent limitations for municipal dischargers, industrial dischargers, industrial users of municipal treatment works, and effluent limitations for toxic substances (applicable to all dischargers).

Standards promulgated or proposed by EPA under 40 CFR, Parts 402 through 699, prescribe effluent limitation guidelines for existing sources, standards of performance for new sources, and pretreatment standards for new and existing sources. Effluent limitations and new source performance standards apply to discharges made directly into receiving bodies of water. The new standards require best available technology (BAT) and are to be used by the states when issuing NPDES permits for all sources 18 months after they are made final by EPA. Pretreatment standards apply to waste streams from industrial sources that are sent to publicly owned treatment works (POTW) for final treatment. These regulations are meant to protect the POTW from any materials that would either harm the treatment facility or pass through untreated. They are to be enforced primarily by the local POTW. These standards are applicable to particular classes of point-sources and pertain to discharges into navigable waters without regard to the quality of the receiving water. Standards are specific for numerous subcategories under each point-source category.

Limitations based upon application of the best practicable control technology currently available (BPT) apply to existing point-sources and should have been achieved by July 1, 1977. Limitations based upon application of the BATEA (Best Available Technology Economically Achievable) that will result in reasonable further progress toward elimination of discharges had to be achieved by July 1, 1984.

Clean Water Act of 1977 The 1977 Clean Water Act directed EPA to review all BAT guidelines for conventional pollutants in those industries not already covered.

On August 23, 1978 (43 FR 37570), the EPA proposed a new approach to the control of conventional pollutants by effluent guideline limitations. The new guidelines were known as best conventional pollutants control technology (BCT). These guidelines replaced the existing BAT limitations, which were determined to be unreasonable for certain categories of pollutants.

In order to determine if BCT limitations would be necessary, the cost effectiveness of conventional pollutant reduction to BAT levels beyond BPT levels had to be determined and compared to the cost of removal of this same amount of pollutant by a publicly owned treatment works of similar capacity. If it was equally cost-effective for the industry to achieve the reduction required for meeting the BAT limitations as the POTW, then the BCT limit was made equal to the BAT level. When this test was applied, the BAT limitation set for certain categories were found to be unreasonable. In these subcategories EPA proposed to remove the BAT limitations and revert to the BPT limitations until BCT control levels could be formulated.

Control of Toxic Pollutants Since the early 1980s, EPA's water-quality standards guidance placed increasing importance on toxic pollutant control. The Agency urged states to adopt criteria into their standards for the priority toxic pollutants, particularly those for which EPA had published criteria guidance. EPA also provided guidance to help and support state adoption of toxic pollutant standards with the *Water Quality Standards Handbook* (1983) and the *Technical Support Document for Water Quality Toxics Control* (1985 and 1991).

Despite EPA's urging and guidance, state response was disappointing. A few states adopted large numbers of numeric toxic pollutant criteria, primarily for the protection of aquatic life. Most other states adopted few or no water-quality criteria for priority toxic pollutants. Some relied on "free from toxicity" criteria and so-called "action levels" for toxic pollutants or occasionally calculated site-specific criteria. Few states addressed the protection of human health by adopting numeric human health criteria.

State development of case-by-case effluent limits using procedures that did not rely on the statewide adoption of numeric criteria for the priority toxic pollutants frustrated Congress. Congress perceived that states were failing to aggressively address toxics and that EPA was not using its oversight role to push the states to move more quickly and comprehensively. Many in Congress believed that these delays undermined the effectiveness of the Act's framework.

1987 CWA Amendments In 1987, Congress, unwilling to tolerate further delays, added Section 303 (c) (2) (B) to the CWA. The Section provided that, whenever a state reviews water-quality standards or revises or adopts new standards, the state had to adopt criteria for all toxic pollutants listed pursuant to Section 307 (a) (1) of the Act for which criteria have been published under Section 304 (a), the discharge or presence of which in the affected waters could reasonably be expected to interfere with those designated uses adopted by the state, as necessary to support such designated uses. Such criteria had to be specific numerical criteria for such toxic pollutants. When such numerical criteria are not available, wherever a state reviews water-quality standards, or revises or adopts new standards, the state has to adopt criteria based on biological monitoring or assessment methods consistent with information published pursuant to Section 304 (a) (8). Nothing in this Section was to be construed to limit or delay the use of effluent limitations or other permit conditions based on or involving biological monitoring or assessment methods or previously adopted numerical criteria.

In response to this new Congressional mandate, EPA redoubled its efforts to promote and assist state adoption of numerical water-quality standards for priority toxic pollutants. EPA's efforts included the development and issuance of guidance to the states on acceptable implementation procedures. EPA attempted to provide the maximum flexibility in its options that complied not only with the express statutory language but also with the ultimate congressional objective: prompt adoption of numeric toxic pollutant criteria. The Agency believed that flexibility was important so that each state could comply with Section 303 (c) (2) (B) within its resource constraints. EPA distributed final guidance on December 12, 1988. This guidance was similar to earlier drafts available for review by the states. The availability of the guidance was published in the *Federal Register* on January 5, 1989 (54 *FR* 346).

The structure of Section 303 (c) is to require states to review their water-quality standards at least once each three-year period. Section 303 (c) (2) (B) instructs states to include reviews for toxics criteria whenever they initiate a triennial review. EPA initially looked at February 4, 1990, the 3-year anniversary of the 1987 CWA amendments, as a convenient point to index state compliance. The April 17, 1990 *Federal Register* Notice (55 *FR* 14350) used this index point for the preliminary assessment of state compliance. However, some states were very nearly completing their state administrative processes for ongoing reviews when the 1987 amendments were enacted and could not legally amend those proceedings to address additional toxics criteria. Therefore, in the interest of fairness, and to provide such states a full 3-year review period, EPA's FY 1990 Agency Operating Guidance provided that states should complete adoption of the numeric criteria to meet Section 303 (c) (2) (B) by September 30, 1990.

Section 303 (c) does not provide penalties for states that do not complete timely water-quality standard reviews. In no previous case had an EPA Administrator found that state failure to complete a review within three years jeopardized the public health or welfare to such an extent that promulgation of Federal standards pursuant to Section 303 (c) (4) (B) was justified. However, the pre-1987 CWA never mandated state adoption of priority toxic pollutants or other specific criteria. EPA relied on its water-quality standards regulation (40 CFR 131.11) and its criteria and program guidance to the states on appropriate parametric coverage in state water quality standards, including toxic pollutants. With Congressional concern exhibited in the legislative history for the 1987 Amendments regarding undue delays by states and EPA, and because states have been explicitly required to adopt numeric criteria for appropriate priority toxic pollutants since 1983, the Agency is proceeding to promulgate Federal standards pursuant to Section 303 (c) (4) (B) of the CWA and 40 CFR 131.22 (b).

States have made substantial recent progress in the adoption, and EPA approval, of toxic pollutant water-quality standards. Furthermore, virtually all states have at least proposed new toxics criteria for priority toxic pollutants since Section 303 (c) (2) (B) was added to the CWA in February of 1987. Unfortunately, not all such state proposals address, in a comprehensive manner, the requirements of Section 303 (c) (2) (B). For example, some states have proposed to adopt criteria to protect aquatic life, but not human health; other states have proposed human health criteria that do not address major exposure pathways (such as the combination of both fish consumption and drinking water). In addition, in some cases final adoption of proposed state toxics criteria that would be approved by EPA has been substantially delayed due to controversial and difficult issues associated with the toxic pollutant criteria adoption process.

Biological Criteria While the overall mandate of the Clean Water Act may now be more clearly stated and understood, the tools needed are still under development, and their full application is being worked out. The direction is towards a more comprehensive approach to water quality protection, which might be more appropriately termed "water resource protection" to encompass the living resources and their habitat along with the water itself.

In 1991, EPA directed states to adopt biological criteria into their water-quality standards by September 30, 1993. To assist the states, EPA issued its "Policy on the Use of Biological Assessments and Criteria in the Water-Quality Program," which sets forth the key policy directions governing the shift to the use of biological criteria:

- "Biological surveys shall be fully integrated with toxicity and chemical-specific assessment methods in state water-quality programs."
- "Biological surveys should be used together with whole-effluent and ambient toxicity testing, and chemical-specific analyses to assess the attainment/nonattainment of designated aquatic life uses in state water-quality standards."
- "If any one of the three assessment methods demonstrate that water-quality standards are not attained, it is EPA's policy that appropriate action should be taken to achieve attainment, including use of regulatory authority" (the independent applicability policy).
- "States should designate aquatic life uses that appropriately address biological integrity and adopt biological criteria necessary to protect those uses."

These policy statements are founded on the existing language and authorities in Clean Water Act Sections 303 (c) (2) (A) and (B). EPA defined biological criteria as "numerical values or narrative expressions used to describe the expected structure and function of the aquatic community."

Most states currently conduct biological surveys. These consist of the collection and analysis of resident aquatic-community data and a subsequent determination of the aquatic community's structure and function. A limiting factor in the number of surveys conducted is simply the funding to support field sampling. Most states also take their survey data through the next level of analysis, which is a biological assessment, in which the biological condition of the water body is evaluated. A state needs to conduct a biological assessment to justify designated waters as having uses less than the Clean Water Act goal of "fishable/swimmable" [Sec. 101 (a) (2)].

Implementing biological criteria requires that the state establish what the expected condition of a biological community should be. This expected condition (or reference condition) is based on measurements at either unimpacted sites or sites that are minimally impacted by human activities. A key element of developing and adopting biological criteria is developing a set of metrics (biological measurements) and indices (summations of those metrics) that are sensitive to reflecting the community changes that occur as a result of human perturbation. Metrics may include measures of species richness, percentages of species of a particular feeding type, and measures of species abundance and condition. The development of metrics and indices have been major technical advances that have effectively brought the field to the point of implementing biological integrity measures.

Aside from the need for additional monitoring and data as a basis for biological criteria, the largest impediment is currently related to the question of how or whether biological criteria should be translated directly into NPDES permit requirements. A strict reading of the NPDES regulations leads some individuals to conclude that every water-quality standard potentially affected by a discharge must have a specific effluent limit. In the case of biological criteria, the direct translation isn't always possible. The preferred approach is to use biological criteria as a primary means to identify impaired waters that will then need additional study. Appropriate discharge controls can then be applied.

The other area of contention in adopting biocriteria is the EPA policy of "independent applicability." This policy recognizes that chemical-specific criteria, toxicity testing (WET tests), and biological criteria each have unique as well as overlapping attributes, limitations, and program applications. No single approach is superior to another; rather, the approaches are complementary. When any one of these approaches indicates that water quality is impaired, appropriate regulatory action is needed. Critics of this approach most frequently cite biological criteria as the superior, or determining, measure and would use it to override an exceedance of chemical-specific criteria.

EPA and many states are now moving towards a watershed or basin management approach to water management. This is a holistic approach that looks at the multiple stresses and activities that affect a basin and evaluates these effects in the context of the survival of ecological systems. Biological criteria are recognized by states as a necessary tool for detecting impacts to important aquatic resources that would otherwise be missed, particularly those caused by nonpoint source activities, and for defining the desired endpoint of environmental restoration activities.

To assist states, EPA has issued programmatic guidance (*Biological Criteria: National Program Guidance for Surface Waters,* April 1990; *Procedures for Initiating Narrative Biological Criteria,* October 1992). In addition, EPA will be issuing over the next couple of years technical guidance specific to developing biological criteria for streams and small rivers, lakes and reservoirs, estuaries, and wetlands.

Metal Bioavailability and Toxicity Another area of policy and regulatory change that bears directly on questions of biological integrity is the application of toxic-metal water-quality criteria. EPA is in the midst of reconsidering its approach to implementing toxic metals criteria. This was prompted in part by the difficulty that some dischargers are having in meeting the state ambient water-quality criteria

for metals, which generally are expressed as total recoverable metals (a measurement that includes the metal dissolved in water plus metal that becomes dissolved when the sample is treated with acid). At issue is whether the criteria can be expressed in a form that more accurately addresses the toxicity of the metal to aquatic life, thereby providing the desired level of aquatic life protection, while allowing more leeway in the total amount of metal discharged. This is a technically complex issue that will require long-term research even if short-term solutions are implemented.

The bioavailability, and hence the toxicity, of metal depends on the physical and chemical form of the metal, which in turn depends on the chemical characteristics of the surrounding water. The dissolved form of the metal is generally viewed as more bioavailable and therefore more toxic than the particulate form. Particulate matter and dissolved organic matter can bind the metal, making it less bioavailable. What is not well known or documented is the various chemical transformations that occur both within the effluent stream and when the effluent reaches and mixes with the receiving water. Metal that is not bioavailable in the effluent may become bioavailable under ambient chemical conditions.

The NPDES regulations (40 CFR 122.45) require effluent limits to be expressed as total recoverable metal. This requirement makes sense as a means to monitor and regulate both the total metal loading and also the effectiveness of wastewater treatment that involves chemical precipitation of the metal.

From the perspective of ecological integrity called for in the Clean Water Act, any adjustment to the implementation of toxic metals criteria needs to be integrated with both sediment criteria and biological criteria to provide ecosystem protection envisioned by the Act.

Regulatory Direction EPA and states are directed by the Clean Water Act to develop programs to meet the Act's stated objective: "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters" [Sec. 101 (a)]. Efforts to date have emphasized "clean water" quite literally, by focusing on the chemical makeup of discharges and their compliance with chemical water-quality standards established for surface water bodies. These programs have successfully addressed many water-pollution problems, but they are not sufficient to identify and address all of them. A large gap in the current regulatory scheme is the absence of a direct measure of the condition of the biological resources that we are intending to protect (the biological integrity of the water body). Without such a measure it will be difficult to determine whether our water-management approaches are successful in meeting the intent of the Act. Taken together, chemical, physical, and biological integrity are equivalent to the "ecological integrity" of a water body. It is highly likely the future will see interpretation of biological integrity and ecological integrity, and the management of ecological systems, assuming a much more prominent role in water-quality management.

UNITED STATES SOLID WASTE LEGISLATION AND REGULATIONS

Much of the current activity in the field of solid waste management, especially with respect to hazardous wastes and resources recovery, is a direct consequence of recent legislation. Therefore, it is important to review the principal legislation that has affected the entire field of solid-waste management.

What follows is a brief review of existing legislation that affects the management of solid wastes. The actual legislation must be consulted for specific detail. Implementation of the legislation is accomplished through regulations adopted by federal, states, and local agencies. Because these regulations are revised continuously, they must be monitored continuously, especially when design and construction work is to be undertaken.

Rivers and Harbors Act, 1899 Passed in 1899, the Rivers and Harbor Act directed the U.S. Army Corps of Engineers to regulate the dumping of debris in navigable waters and adjacent lands.

Solid Waste Disposal Act, 1965 Modern solid-waste legislation dates from 1965, when the Solid Waste Disposal Act, Title II of Public Law 88-272, was enacted by Congress. The principal intent of this act was to promote the demonstration, construction, and application of solid waste management and resource-recovery systems that preserve and enhance the quality of air, water, and land resources.

National Environmental Policy Act, 1969 The National Environmental Policy Act (NEPA) of 1969 was the first federal act that required coordination of federal projects and their impacts with the nation's resources. The act specified the creation of Council on Environmental Quality in the Executive Office of the President. This body has the authority to force every federal agency to submit to the council an environmental impact statement on every activity or project which it may sponsor or over which it has jurisdiction.

Resource Recovery Act, 1970 The Solid Waste Disposal Act of 1965 was amended by Public Law 95-512, the Resources Recovery Act of 1970. This act directed that the emphasis of the national solid-waste-management program should be shifted from disposal as its primary objective to that of recycling and reuse of recoverable materials in solid wastes or the conversion of wastes to energy.

Resource Conservation and Recovery Act, 1976 RCRA is the primary statute governing the regulation of solid and hazardous waste. It completely replaced the Solid Waste Disposal Act of 1965 and supplemented the Resource Recovery Act of 1970; RCRA itself was substantially amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA). The principal objectives of RCRA as amended are to:

- Promote the protection of human health and the environment from potential adverse effects of improper solid and hazardous waste management
- Conserve material and energy resources through waste recycling and recovery
- Reduce or eliminate the generation of hazardous waste as expeditiously as possible

To achieve these objectives, RCRA authorized EPA to regulate the generation, treatment, storage, transportation, and disposal of hazardous wastes. The structure of the national hazardous waste regulatory program envisioned by Congress is laid out in Subtitle C of RCRA (Sections 3001 through 3019), which authorized EPA to:

- Promulgate standards governing hazardous waste generation and management
- Promulgate standards for permitting hazardous waste treatment, storage, and disposal facilities
- Inspect hazardous waste management facilities
- Enforce RCRA standards
- Authorize states to manage the RCRA Subtitle C program, in whole or in part, within their respective borders, subject to EPA oversight

Federal RCRA hazardous waste regulations are set forth in 40 CFR Parts 260 through 272. The core of the RCRA regulations establishes the "cradle to grave" hazardous waste regulatory program through seven major sets of regulations:

- Identification and listing of regulated hazardous wastes (Part 261)
- Standards for generators of hazardous waste (Part 262)
- Standards for transporters of hazardous waste (Part 263)
- Standards for owners/operators of hazardous waste treatment, storage, and disposal facilities (Parts 264, 265, and 267)
- Standards for the management of specific hazardous wastes and specific types of hazardous waste management facilities (Part 266)
- Land disposal restriction standards (Part 268)
- Requirements for the issuance of permits to hazardous waste facilities (Part 270)
- Standards and procedures for authorizing state hazardous waste programs to be operated in lieu of the federal program (Part 271)

EPA, under Section 3006 of RCRA, may authorize a state to administer and enforce a state hazardous waste program in lieu of the federal Subtitle C program. To receive authorization, a state program must:

- Be equivalent to the federal Subtitle C program
- Be consistent with, and no less stringent than, the federal program and other authorized state programs
- Provide adequate enforcement of compliance with Subtitle C requirements

Toxic Substances Control Act, 1976 The two major goals of the Toxic Substances Control Act (TSCA), passed by Congress in

1976, are (1) the acquisition of sufficient information to identify and evaluate potential hazards from chemical substances and (2) the regulation of the manufacture, processing, distribution, use, and disposal of any substance that presents an unreasonable risk of injury to health of the environment.

Under TSCA, the EPA has issued a ban on the manufacture, processing, and distribution of products containing PCBs. Exporting of PCB has also been banned. TSCA also required that PCB mixtures containing more than 50 ppm PCBs must be disposed of in an acceptable incinerator or chemical waste landfill. All PCB containers or products containing PCBs had to be clearly marked and records maintained by the operator of each facility handling at least 45 kilograms of PCB. These records include PCBs in use in transformers and capacitors, PCBs in transformers and capacitors removed from service, PCBs stored for disposal, and a report on the ultimate disposal of the PCBs.

TSCA also placed restrictions on the use of chlorofluorocarbons, asbestos, and fully halogenated chlorofluoroalkanes such as aerosol propellants.

Regulatory Direction There is no doubt that pollution prevention continues to be the regulatory direction. The development of new and more efficient processes and waste minimization technologies will be essential to support this effort.

POLLUTION PREVENTION

This subsection is drawn in part from "Pollution Prevention Overview," prepared by B. Wainwright and L. Theodore, copyrighted, 1993.

FURTHER READING: American Society of Testing and Materials, *Standard Guide for Industrial Source Reduction,* draft copy dated June 16, 1992. American Society of Testing and Materials, *Pollution Prevention, Reuse, Recycling and Environmental Efficiency,* June, 1992. California Department of Health Services, *Economic Implications of Waste Reduction, Recycling, Treatment, and Disposal of Hazardous Wastes: The Fourth Biennial Report,* California, 1988. Citizen's Clearinghouse for Hazardous Waste, *Reduction of Hazardous Waste: The Only Serious Management Option,* Falls Church, CCHW, 1986. Congress of the United States. Office of Technology Assessment, *Serious Reduction of Hazardous Waste: For Pollution Prevention and Industrial Efficiency,* Washington, D.C., GPO, 1986. Friedlander, S., "Pollution Prevention—Implications for Engineering Design, Research, and Education," *Environment,* May 1989, p. 10. Theodore, L. and Y. McGuinn, *Pollution Prevention,* New York, Van Nostrand Reinhold, 1992. Theodore, L. and R. Allen, *Pollution Prevention: An ETS Theodore Tutorial,* Roanoke, VA, ETS International, Inc., 1994. Theodore, L., *A Citizen's Guide to Pollution Prevention,* East Williston, NY, 1993. United States EPA, *Facility Pollution Prevention Guide.* (EPA/600/R-92/088), Washington, D.C., May 1992. United States EPA, "Pollution Prevention Fact Sheets," Washington, D.C., GPO, 1991. United States EPA, *1987 National Biennial RCRA Hazardous Waste Report—Executive Summary,* Washington, D.C., GPO, 1991. United States EPA, Office of Pollution Prevention, *Report on the U.S. Environmental Protection Agency's Pollution Prevention Program,* Washington, D.C., GPO, 1991. World Wildlife Fund, *Getting at the Source—Executive Summary,* 1991.

INTRODUCTION

The amount of waste generated in the United States has reached staggering proportions; according to the United States Environmental Protection Agency (EPA), 250 million tons of solid waste alone are generated annually. Although both the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Act (HSWA) encourage businesses to minimize the wastes they generate, the majority of the environmental protection efforts are still centered around treatment and pollution clean-up.

The passage of the Pollution Prevention Act of 1990 has redirected industry's approach to environmental management; pollution prevention has now become the environmental option of this decade and the 21st century. Whereas typical waste-management strategies concentrate on "end-of-pipe" pollution control, pollution prevention attempts to handle waste at the source (i.e., source reduction). As waste handling and disposal costs increase, the application of pollution prevention measures is becoming more attractive than ever before. Industry is currently exploring the advantages of multimedia waste reduction and developing agendas to *strengthen* environmental design while *lessening* production costs.

There are profound opportunities for both industry and the individual to prevent the generation of waste; indeed, pollution prevention is today primarily stimulated by economics, legislation, liability concerns, and the enhanced environmental benefit of managing waste at the source. The Pollution Prevention Act of 1990 has established pollution prevention as a national policy, declaring that "waste should be prevented or reduced at the source wherever feasible, while pollution that cannot be prevented should be recycled in an environmentally safe manner" (Ref. 1). The EPA's policy establishes the following hierarchy of waste management:

1. Source reduction
2. Recycling/reuse
3. Treatment
4. Ultimate disposal

The hierarchy's categories are prioritized so as to promote the examination of each individual alternative prior to the investigation of subsequent options (i.e., the most preferable alternative should be thoroughly evaluated before consideration is given to a less accepted option). Practices that decrease, avoid, or eliminate the generation of waste are considered source reduction and can include the implementation of procedures as simple and economical as good housekeeping. Recycling is the use, reuse, or reclamation of wastes and/or materials that may involve the incorporation of waste recovery techniques (e.g., distillation, filtration). Recycling can be performed at the facility (i.e., on-site) or at an off-site reclamation facility. Treatment involves the destruction or detoxification of wastes into nontoxic or less toxic materials by chemical, biological, or physical methods, or any combination of these control methods. Disposal has been included in the hierarchy because it is recognized that residual wastes will exist; the EPA's so-called "ultimate disposal" options include landfilling, land farming, ocean dumping, and deep-well injection. However, the term *ultimate disposal* is a misnomer, but is included here because of its adaptation by the EPA.

Table 25-8 provides a rough timetable demonstrating the United States' approach to waste management. Note how waste management has begun to shift from pollution *control*-driven activities to pollution *prevention* activities.

The application of waste-management practices in the United States has recently moved toward securing a new pollution prevention ethic. The performance of pollution prevention assessments and their subsequent implementation will encourage increased activity into methods that will further aid in the reduction of hazardous wastes. One of the most important and propitious consequences of the pollution-prevention movement will be the development of life-cycle design and standardized life-cycle cost-accounting procedures. These two consequences are briefly discussed in the two paragraphs that follow. Additional information is provided in a later subsection.

TABLE 25-8 Waste Management Timetable

Prior to 1945	No control
1945–1960	Little control
1960–1970	Some control
1970–1975	Greater control (EPA is founded)
1975–1980	More sophisticated control
1980–1985	Beginning of waste-reduction management
1985–1990	Waste-reduction management
1990–1995	Formal pollution prevention programs (Pollution Prevention Act)
1995–2000	Widespread acceptance of pollution prevention
After 2000	???

The key element of life-cycle design is Life-Cycle Assessment (LCA). LCA is generally envisioned as a process to evaluate the environmental burdens associated with the cradle-to-grave life cycle of a product, process, or activity. A product's life cycle can be roughly described in terms of the following stages:

1. Raw material
2. Bulk material processing
3. Production
4. Manufacturing and assembly
5. Use and service
6. Retirement
7. Disposal

Maintaining an objective process while spanning this life cycle can be difficult given the varying perspective of groups affected by different parts of that cycle. LCA typically does not include any direct or indirect monetary costs or impacts to individual companies or consumers.

Another fundamental goal of life-cycle design is to promote sustainable development at the global, regional, and local levels. There is significant evidence that suggests that current patterns of human and industrial activity on a global scale are not following a sustainable path. Changes to achieve a more sustainable system will require that environmental issues be more effectively addressed in the future. Principles for achieving sustainable development should include (Ref. 2):

1. *Sustainable resource use (conserving resources, minimizing depletion of nonrenewable resources, using sustainable practices for managing renewable resources).* There can be no product development or economic activity of any kind without available resources. Except for solar energy, the supply of resources is finite. Efficient designs conserve resources while also reducing impacts caused by material extraction and related activities. Depletion of nonrenewable resources and overuse of otherwise renewable resources limits their availability to future generations.

2. *Maintenance of ecosystem structure and function.* This is a principal element of sustainability. Because it is difficult to imagine how human health can be maintained in a degraded, unhealthy natural world, the issue of ecosystem health should be a more fundamental concern. Sustainability requires that the health of all diverse species as well as their interrelated ecological functions be maintained. As only one species in a complex web of ecological interactions, humans cannot separate their success from that of the total system.

3. *Environmental justice.* The issue of environmental justice has come to mean different things to different people. Theodore (Ref. 3) has indicated that the subject of environmental justice contains four key elements that are interrelated: environmental racism, environmental health, environmental equity, and environmental politics. (Unlike many environmentalists, Theodore has contended that only the last issue, politics, is a factor in environmental justice.) A major challenge in sustainable development is achieving both intergenerational and intersocietal environmental justice. Overconsuming resources and polluting the planet in such a way that it enjoins future generations from access to reasonable comforts irresponsibly transfer problems to the future in exchange for short-term gain. Beyond this intergenerational conflict, enormous inequities in the distribution of resources continue to exist between developed and less developed countries. Inequities also occur within national boundaries.

Life cycle is a perspective that considers the true costs of product production and/or services provided and utilized by analyzing the price associated with potential environmental degradation and energy consumption, as well as more customary costs like capital expenditure and operating expenses. Unfortunately, a host of economic and economic-related terms have appeared in the literature. Some of these include total cost assessment, life-cycle costing, and full-cost accounting. Unfortunately, these terms have come to mean different things to different people at different times. In an attempt to remove this ambiguity, the following three economic terms are defined below. The reader is also referred to Fig. 25-1 for additional details.

1. *Traditional costing procedure (TCP).* This accounting procedure *only* takes into account capital and operating (including environmental) costs.

2. *Comprehensive costing procedure (CCP).* The economic procedure includes not only the traditional capital and operating costs but also peripheral costs such as liability, regulatory related expensive, borrowing power, and social considerations.

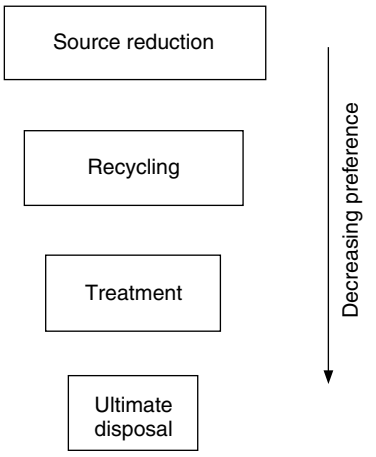


FIG. 25-1 Pollution prevention hierarchy.

3. *Life-cycle costing (LCC).* This type of analysis requires that all the traditional costs of project or product system, from raw-material acquisition to end-result product disposal, be considered.

The TCP approach is relatively simple and can be easily applied to studies involving comparisons of different equipments, different processes, or even parts of processes. CCP has now emerged as the most realistic approach that can be employed in economic project analyses. It is the recommended procedure for pollution-prevention studies. The LCC approach is usually applied to the life-cycle analysis (LCA) of a product or service. It has found occasional application in project analysis.

The remainder of this subsection on pollution prevention will be concerned with providing the reader with the necessary background to understand the meaning of pollution prevention and its useful implementation. Assessment procedures and the economic benefits derived from managing pollution at the source are discussed along with methods of cost accounting for pollution prevention. Additionally, regulatory and nonregulatory methods to promote pollution prevention and overcome barriers are examined, and ethical considerations are presented. By eliminating waste at the source, all can participate in the protection of the environment by reducing the amount of waste material that would otherwise need to be treated or ultimately disposed; accordingly, attention is also given to pollution prevention in both the domestic and business office environments.

POLLUTION-PREVENTION HIERARCHY

As discussed in the introduction, the hierarchy set forth by the USEPA in the Pollution Prevention Act establishes an order to which waste-management activities should be employed to reduce the quantity of waste generated. The preferred method is source reduction, as indicated in Fig. 25-1. This approach actually precedes traditional waste management by addressing the source of the problem prior to its occurrence.

Although the EPA's policy does not consider recycling or treatment as actual pollution prevention methods per se, these methods present an opportunity to reduce the amount of waste that might otherwise be discharged into the environment. Clearly, the definition of pollution prevention and its synonyms (e.g., waste minimization) must be understood to fully appreciate and apply these techniques.

Waste minimization generally considers all of the methods in the EPA hierarchy (except for disposal) appropriate to reduce the volume or quantity of waste requiring disposal (i.e., source reduction). The definition of *source reduction* as applied in the Pollution Prevention Act, however, is "any practice that reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream

or otherwise released into the environment . . . prior to recycling, treatment or disposal" (Ref. 1). Source reduction reduces the amount of waste generated; it is therefore considered true pollution prevention and has the highest priority in the EPA hierarchy.

Recycling (or reuse) refers to the use (or reuse) of materials that would otherwise be disposed of or treated as a waste product. A good example is a rechargeable battery. Wastes that cannot be directly reused may often be recovered on-site through methods such as distillation. When on-site recovery or reuse is not feasible due to quality specifications or the inability to perform recovery on-site, off-site recovery at a permitted commercial recovery facility is often a possibility. Such management techniques are considered secondary to source reduction and should only be used when pollution cannot be prevented.

The treatment of waste is the third element of the hierarchy and should be utilized only in the absence of feasible source reduction or recycling opportunities. Waste treatment involves the use of chemical, biological, or physical processes to reduce or eliminate waste material. The incineration of wastes is included in this category and is considered "preferable to other treatment methods (i.e., chemical, biological, and physical) because incineration can permanently destroy the hazardous components in waste materials" (Ref. 4). It can also be employed to reduce the volume of waste to be treated.

Of course, several of these pollution-prevention elements are used by industry in combination to achieve the greatest waste reduction. Residual wastes that cannot be prevented or otherwise managed are then disposed of only as a last resort.

Figure 25-2 provides a more detailed schematic representation of the two preferred pollution prevention techniques (i.e., source reduction and recycling).

MULTIMEDIA ANALYSIS AND LIFE-CYCLE ANALYSIS

Multimedia Analysis In order to properly design and then implement a pollution prevention program, sources of all wastes must be fully understood and evaluated. A multimedia analysis involves a multifaceted approach. It must not only consider one waste stream but all potentially contaminant media (e.g., air, water, land). Past waste-management practices have been concerned primarily with treatment. All too often, such methods solve one waste problem by transferring a contaminant from one medium to another (e.g., air stripping); such waste shifting is *not* pollution prevention or waste reduction.

Pollution prevention techniques must be evaluated through a thorough consideration of all media, hence the term multimedia. This approach is a clear departure from previous pollution treatment or control techniques where it was acceptable to transfer a pollutant from one source to another in order to solve a waste problem. Such strategies merely provide short-term solutions to an ever increasing problem. As an example, air pollution control equipment prevents or reduces the discharge of waste into the air but at the same time can produce a solid (hazardous) waste problem.

Life-Cycle Analysis The aforementioned multimedia approach to evaluating a product's waste stream(s) aims to ensure that the treatment of one waste stream does not result in the generation or increase in an additional waste output. Clearly, impacts resulting during the production of a product or service must be evaluated over its entire history or life cycle. This life-cycle analysis or total systems approach (Ref. 3) is crucial to identifying opportunities for improvement. As described earlier, this type of evaluation identifies "energy use, material inputs, and wastes generated during a product's life: from extraction and processing of raw materials to manufacture and transport of a product to the marketplace and finally to use and dispose of the product" (Ref. 5).

During a forum convened by the World Wildlife Fund and the Conservation Foundation in May 1990, various steering committees recommended that a three-part life-cycle model be adopted. This model consists of the following:

1. An inventory of materials and energy used, and environmental releases from all stages in the life of a product or process
2. An analysis of potential environmental effects related to energy use and material resources and environmental releases
3. An analysis of the changes needed to bring about environmental improvements for the product or process under evaluation

Traditional cost analysis often fails to include factors relevant to future damage claims resulting from litigation, the depletion of nat-

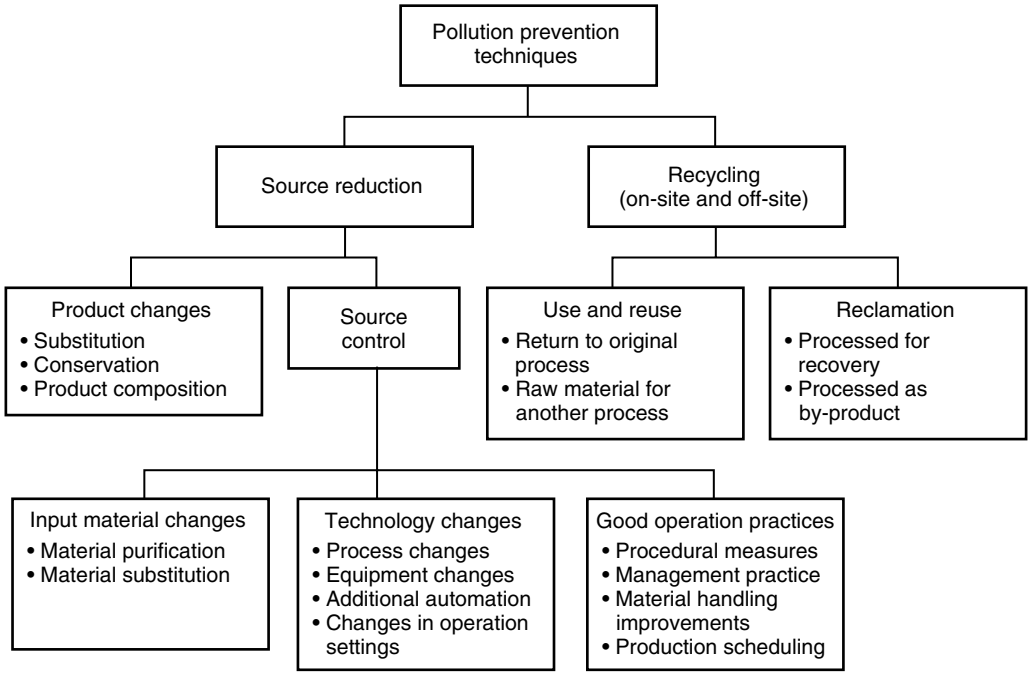


FIG. 25-2 Pollution prevention techniques.

ural resources, the effects of energy use, and the like. As such, waste-management options such as treatment and disposal may appear preferential if an overall life-cycle cost analysis is not performed. It is evident that environmental costs from cradle to grave have to be evaluated together with more conventional production costs to accurately ascertain genuine production costs. In the future, a total systems approach will most likely involve a more careful evaluation of pollution, energy, and safety issues. For example, if one was to compare the benefits of coal versus oil as a fuel source for an electric power plant, the use of coal might be considered economically favorable. In addition to the cost issues, however, one must be concerned with the environmental effects of coal mining (e.g., transportation and storage prior to use as a fuel). Society often has a tendency to overlook the fact that there are serious health and safety matters (e.g., miner exposure) that must be considered along with the effects of fugitive emissions. When these effects are weighed alongside standard economic factors, the full cost benefits of coal usage may be eclipsed by environmental costs. Thus, many of the economic benefits associated with pollution prevention are often unrecognized due to inappropriate cost-accounting methods. For this reason, economic considerations are detailed later.

POLLUTION-PREVENTION ASSESSMENT PROCEDURES

The first step in establishing a pollution prevention program is the obtainment of management commitment. This is necessary given the inherent need for project structure and control. Management will determine the amount of funding allotted for the program as well as specific program goals. The data collected during the actual evaluation is then used to develop options for reducing the types and amounts of waste generated. Figure 25-3 depicts a systematic approach that can be used during the procedure. After a particular waste stream or area of concern is identified, feasibility studies are performed involving both economic and technical considerations. Finally, preferred alternatives are implemented. The four phases of the assessment (i.e., planning and organization, assessment, feasibility, and implementation) are introduced in the following subsections. Sources of additional information as well as information on industrial programs is also provided in this section.

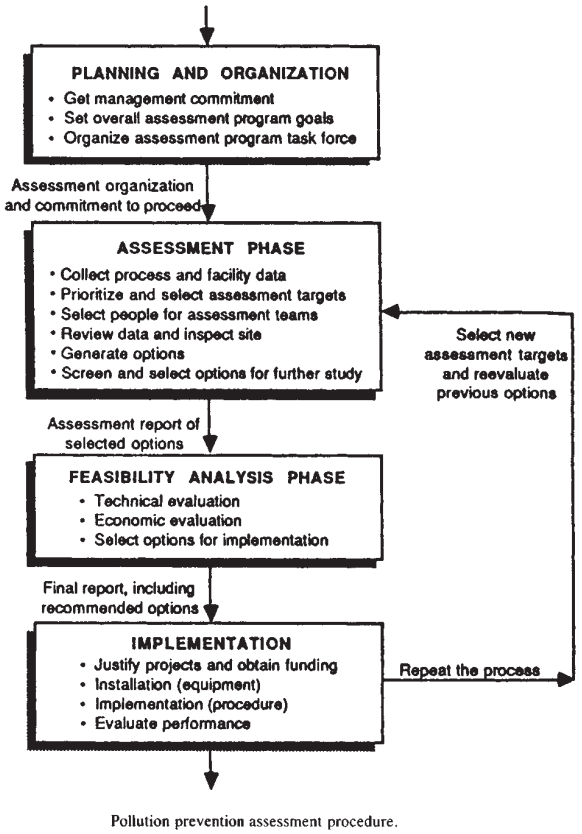


FIG. 25-3 Pollution prevention assessment procedure.

Planning and Organization The purpose of this phase is to obtain management commitment, define and develop program goals, and assemble a project team. Proper planning and organization are crucial to the successful performance of the pollution-prevention assessment. Both managers and facility staff play important roles in the assessment procedure by providing the necessary commitment and familiarity with the facility, its processes, and current waste-management operations. It is the benefits of the program, including economic advantages, liability reduction, regulatory compliance, and improved public image that often leads to management support.

Once management has made a commitment to the program and goals have been set, a program task force is established. The selection of a team leader will be dependent upon many factors including their ability to effectively interface with both the assessment team and management staff.

The task force must be capable of identifying pollution reduction alternatives as well as be cognizant of inherent obstacles to the process. Barriers frequently arise from the anxiety associated with the belief that the program will negatively affect product quality or result in production losses. According to an EPA survey, 30 percent of industry comments responded that they were concerned that product quality would decline if waste minimization techniques were implemented (Ref. 6). As such, the assessment team, and the team leader in particular, must be ready to react to these and other concerns (Ref. 2).

Assessment Phase The assessment phase aims to collect data needed to identify and analyze pollution-prevention opportunities. Assessment of the facility's waste-reduction needs includes the examination of hazardous waste streams, process operations, and the identification of techniques that often promise the reduction of waste generation. Information is often derived from observations made during a facility walk-through, interviews with employees (e.g., operators, line workers), and review of site or regulatory records. One professional organization suggests the following information sources be reviewed, as available (Ref. 7):

1. Product design criteria
2. Process flow diagrams for all solid waste, wastewater, and air emissions sources
3. Site maps showing the location of all pertinent units (e.g., pollution-control devices, points of discharge)
4. Environmental documentation, including: Material Safety Data Sheets (MSDS), military specification data, permits (e.g., NPDES, POTW, RCRA), SARA Title III reports, waste manifests, and any pending permits or application information
5. Economic data, including: cost of raw material management; cost of air, wastewater, and hazardous waste treatment; waste management operating and maintenance costs; and waste disposal costs
6. Managerial information: environmental policies and procedures; prioritization of waste-management concerns; automated or computerized waste-management systems; inventory and distribution procedures; maintenance scheduling practices; planned modifications or revisions to existing operations that would impact waste-generation activities; and the basis of source reduction decisions and policies

The use of process flow diagrams and material balances are worthwhile methods to quantify losses or emissions and provide essential data to estimate the size and cost of additional equipment, other data to evaluate economic performance, and a baseline for tracking the progress of minimization efforts (Ref. 3). Material balances should be applied to individual waste streams or processes and then utilized to construct an overall balance for the facility. Details on these calculations are available in the literature (Ref. 8). In addition, an introduction to this subject is provided in the next section.

The data collected is then used to prioritize waste streams and operations for assessment. Each waste stream is assigned a priority

based on corporate pollution-prevention goals and objectives. Once waste origins are identified and ranked, and potential methods to reduce the waste stream are evaluated. The identification of alternatives is generally based on discussions with the facility staff; review of technical literature; and contacts with suppliers, trade organizations, and regulatory agencies.

Alternatives identified during this phase of the assessment are evaluated using screening procedures so as to reduce the number of alternatives requiring further exploration during the feasibility analysis phase. The criteria used during this screening procedure include: cost-effectiveness; implementation time; economic, compliance, safety and liability concerns; waste-reduction potential; and whether the technology is proven (Refs. 4, 8). Options that meet established criteria are then examined further during the feasibility analysis.

Feasibility Analysis The selection procedure is performed by an evaluation of technical and economic considerations. The technical evaluation determines whether a given option will work as planned. Some typical considerations follow:

1. Safety concerns
2. Product quality impacts or production delays during implementation
3. Labor and/or training requirements
4. Creation of new environmental concerns
5. Waste reduction potential
6. Utility and budget requirements
7. Space and compatibility concerns

If an option proves to be technically ineffective or inappropriate, it is deleted from the list of potential alternatives. Either following or concurrent with the technical evaluation, an economic study is performed, weighing standard measures of profitability such as payback period, investment returns, and net present value. Many of these costs (or, more appropriately, cost savings) may be substantial yet are difficult to quantify. (Refer to *Economic Considerations Associated with Pollution Prevention.*)

Implementation The findings of the overall assessment are used to demonstrate the technical and economic worthiness of program implementation. Once appropriate funding is obtained, the program is implemented not unlike any other project requiring new procedures or equipment. When preferred waste-pollution-prevention techniques are identified, they are implemented and should become part of the facility's day-to-day management and operation. Subsequent to the program's execution, its performance should be evaluated in order to demonstrate effectiveness, generate data to further refine and augment waste-reduction procedures, and maintain management support.

It should be noted that waste reduction, energy conservation, and safety issues are interrelated and often complementary to each other. For example, the reduction in the amount of energy a facility consumes usually results in reduced emissions associated with the generation of power. Energy expenditures associated with the treatment and transport of waste are similarly reduced when the amount of waste generated is lessened; at the same time, worker safety is elevated due to reduced exposure to hazardous materials. However, this not always the case. Addition of air-pollution control systems at power plants decreases net power output due to the power consumed by the equipment. This in turn requires more fuel to be combusted for the same power exported to the grid. This additional fuel increases pollution from coal mining, transport, ash disposal, and the like. In extreme cases, very high recovery efficiencies for some pollutants can raise, not lower, total emissions. Seventy percent removal might produce a 2 percent loss in power output; 90 percent recovery could lead to a 3 percent loss; 95 percent, a 5 percent loss; 99 percent, a 10 percent loss, and so on. The point to be made is that pollution control is generally not a "free lunch."

Sources of Information The successful development and implementation of any pollution prevention program is not only dependent on a thorough understanding of the facility's operations but also requires an intimate knowledge of current opportunities and advances in the field. In fact, 32 percent of industry respondents to an EPA survey identified the lack of technical information as a major factor delaying or preventing the implementation of a waste-minimization program (Ref. 6). One of EPA's positive contributions has been the development of a national Pollution Prevention Information Clearinghouse (PPIC) and the Pollution Prevention Information Exchange System (PIES) to facilitate the exchange of information needed to promote pollution prevention through efficient information transfer (Ref. 2).

PPIC is operated by the EPA's Office of Research and Development and the Office of Pollution Prevention. The clearinghouse is comprised of four elements:

1. Repository, including a hard copy reference library and collection center and an on-line information retrieval and ordering system.
2. PIES, a computerized conduit to databases and document ordering, accessible via modem and personal computer: (703) 506-1025.
3. PPIC uses the RCRA/Superfund and Small Business Ombudsman Hotlines as well as a PPIC technical assistance line to answer pollution-prevention questions, access information in the PPIC, and assist in document ordering and searches. To access PPIC by telephone, call:

   RCRA/Superfund Hotline, (800) 242-9346
   Small Business Ombudsman Hotline, (800) 368-5888
   PPIC Technical Assistance, (703) 821-4800

4. PPIC compiles and disseminates information packets and bulletins and initiates networking efforts with other national and international organizations.

Additionally, the EPA publishes a newsletter entitled *Pollution Prevention News* that contains information including EPA news, technologies, program updates, and case studies. The EPA's Risk Reduction Engineering Laboratory and the Center for Environmental Research Information has published several guidance documents, developed in cooperation with the California Department of Health Services. The manuals supplement generic waste reduction information presented in the EPA's *Waste Minimization Opportunity Assessment Manual* (Ref. 9).

Pollution prevention or waste minimization programs have been established at the State level and as such are good sources of information. Both Federal and State agencies are working with universities and research centers and may also provide assistance. For example, the American Institute of Chemical Engineers has established the Center for Waste Reduction Technologies (CWRT), a program based on targeted research, technology transfer, and enhanced education.

Industry Programs A significant pollution-prevention resource may very well be found with the "competition." Several large companies have established well-known programs that have successfully incorporated pollution-prevention practices into their manufacturing processes. These include, but are not limited to: 3M—Pollution Prevention Pays (3P); Dow Chemical—Waste Reduction Always Pays (WRAP); Chevron—Save Money and Reduce Toxics (SMART); and, the General Dynamics Zero Discharge Program.

Smaller companies can benefit by the assistance offered by these larger corporations. It is clear that access to information is of major importance when implementing efficient pollution-prevention programs. By adopting such programs, industry is affirming pollution prevention's application as a good business practice and not simply a "noble" effort.

ASSESSMENT PHASE MATERIAL BALANCE CALCULATIONS

(The reader is directed to Refs. 4 and 10 for further information.)

One of the key elements of the assessment phase of a pollution prevention program involves mass balance equations. These calculations are often referred to as material balances; the calculations are performed via the conservation law for mass. The details of this often-used law are described below.

The conservation law for mass can be applied to any process or system. The general form of the law follows:

$$\textit{mass in} - \textit{mass out} + \textit{mass generated} = \textit{mass accumulated}$$

This equation can be applied to the total mass involved in a process or to a particular species, on either a mole or mass basis. The conserva-

tion law for mass can be applied to steady-state or unsteady-state processes and to batch or continuous systems. A steady-state system is one in which there is no change in conditions (e.g., temperature, pressure) or rates of flow with time at any given point in the system; the accumulation term then becomes zero. If there is no chemical reaction, the generation term is zero. All other processes are classified as unsteady state.

To isolate a system for study, the system is separated from the surroundings by a boundary or envelope that may either be real (e.g., a reactor vessel) or imaginary. Mass crossing the boundary and entering the system is part of the mass-in term. The equation may be used for any compound whose quantity does not change by chemical reaction or for any chemical element, regardless of whether it has participated in a chemical reaction. Furthermore, it may be written for one piece of equipment, several pieces of equipment, or around an entire process (i.e., a total material balance).

The conservation of mass law finds a major application during the performance of pollution-prevention assessments. As described earlier, a pollution-prevention assessment is a systematic, planned procedure with the objective of identifying methods to reduce or eliminate waste. The assessment process should characterize the selected waste streams and processes (Ref. 11)—a necessary ingredient if a material balance is to be performed. Some of the data required for the material balance calculation may be collected during the first review of site-specific data; however, in some instances, the information may not be collected until an actual site walk-through is performed.

Simplified mass balances should be developed for each of the important waste-generating operations to identify sources and gain a better understanding of the origins of each waste stream. Since a mass balance is essentially a check to make sure that what goes into a process (i.e., the total mass of all raw materials), what leaves the process (i.e., the total mass of the products and by-products), the material balance should be made individually for all components that enter and leave the process. When chemical reactions take place in a system, there is an advantage to doing "elemental balances" for specific chemical elements in a system. Material balances can assist in determining concentrations of waste constituents where analytical test data are limited. They are particularly useful when there are points in the production process where it is difficult or uneconomical to collect analytical data.

Mass-balance calculations are particularly useful for quantifying fugitive emissions such as evaporative losses. Waste stream data and mass balances will enable one to track flow and characteristics of the waste streams over time. Since in most cases the accumulation equals zero (steady-state operation), it can then be assumed that any buildup is actually leaving the process through fugitive emissions or other means. This will be useful in identifying trends in waste/pollutant generation and will also be critical in the task of measuring the performance of implemented pollution prevention options. The result of these activities is a catalog of waste streams that provides a description of each waste, including quantities, frequency of discharge, composition, and other important information useful for material balance. Of course, some assumptions or educated estimates will be needed when it is impossible to obtain specific information.

By performing a material balance in conjunction with a pollution prevention assessment, the amount of waste generated becomes known. The success of the pollution prevention program can therefore be measured by using this information on baseline generation rates (i.e., that rate at which waste is generated without pollution prevention considerations).

BARRIERS AND INCENTIVES TO POLLUTION PREVENTION

As discussed previously, industry is beginning to realize that there are profound benefits associated with pollution prevention including cost effectiveness, reduced liability, enhanced public image, and regulatory compliance. Nevertheless, there are barriers or disincentives identified with pollution prevention. This section will briefly outline both barriers and incentives that may need to be confronted or considered during the evaluation of a pollution prevention program.

Barriers to Pollution Prevention ("The Dirty Dozen") There are numerous reasons why more businesses are not reducing the wastes they generate. The following "dirty dozen" are common disincentives:

1. *Technical limitations.* Given the complexity of present manufacturing processes, waste streams exist that cannot be reduced with current technology. The need for continued research and development is evident.
2. *Lack of information.* In some instances, the information needed to make a pollution-prevention decision may be confidential or is difficult to obtain. In addition, many decision makers are simply unaware of the potential opportunities available regarding information to aid in the implementation of a pollution-prevention program.
3. *Consumer preference obstacles.* Consumer preference strongly affects the manner in which a product is produced, packaged, and marketed. If the implementation of a pollution-prevention program results in the increase in the cost of a product or decreased convenience or availability, consumers might be reluctant to use it.
4. *Concern over product quality decline.* The use of a less hazardous material in a product's manufacturing process may result in decreased life, durability, or competitiveness.
5. *Economic concerns.* Many companies are unaware of the economic advantages associated with pollution prevention. Legitimate concerns may include decreased profit margins or the lack of funds required for the initial capital investment.
6. *Resistance to change.* The unwillingness of many businesses to change is rooted in their reluctance to try technologies that may be unproven or based on a combination of the barriers discussed in this section.
7. *Regulatory barriers.* Existing regulations that have created incentives for the control and containment of wastes are at the same time discouraging the exploration of pollution-prevention alternatives. Moreover, since regulatory enforcement is often intermittent, current legislation can weaken waste-reduction incentives.
8. *Lack of markets.* The implementation of pollution-prevention processes and the production of environmentally friendly products will be of no avail if markets do not exist for such goods. As an example, the recycling of newspaper in the United States has resulted in an overabundance of waste paper without markets prepared to take advantage of this raw material.
9. *Management apathy.* Many managers capable of making decisions to begin pollution-prevention activities, do not realize the potential benefits of pollution prevention.
10. *Institutional barriers.* In an organization without a strong infrastructure to support pollution-prevention plans, waste-reduction programs will be difficult to implement. Similarly, if there is no mechanism in place to hold individuals accountable for their actions, the successful implementation of a pollution-prevention program will be limited.
11. *Lack of awareness of pollution prevention advantages.* As mentioned in reason no. 5, decision makers may merely be uninformed of the benefits associated with pollution reduction.
12. *Concern over the dissemination of confidential product information.* If a pollution-prevention assessment reveals confidential data pertinent to a company's product, fear may exist that the organization will lose a competitive edge with other businesses in the industry.

Pollution-Prevention Incentives ("A Baker's Dozen") Various means exist to encourage pollution prevention through regulatory measures, economic incentives, and technical assistance programs. Since the benefits of pollution prevention can surpass prevention barriers, a "baker's dozen" incentives is presented below:

1. *Economic benefits.* The most obvious economic benefits associated with pollution prevention are the savings that result from the elimination of waste storage, treatment, handling, transport, and disposal. Additionally, less tangible economic benefits are realized in terms of decreased liability, regulatory compliance costs (e.g., permits), legal and insurance costs, and improved process efficiency. Pollution prevention almost always pays for itself, particularly when the time required to comply with regulatory standards is considered. Several of these economic benefits are discussed separately below.

2. *Regulatory compliance.* Quite simply, when wastes are not generated, compliance issues are not a concern. Waste-management costs associated with record keeping, reporting, and laboratory analysis are reduced or eliminated. Pollution prevention's proactive approach to waste management will better prepare industry for the future regulation of many hazardous substances and wastes that are currently unregulated. Regulations have, and will continue to be, a moving target.

3. *Liability reduction.* Facilities are responsible for their wastes from "cradle-to-grave." By eliminating or reducing waste generation, future liabilities can also be decreased. Additionally, the need for expensive pollution liability insurance requirements may be abated.

4. *Enhanced public image.* Consumers are interested in purchasing goods that are safer for the environment, and this demand, depending on how they respond, can mean success or failure for many companies. Business should therefore be sensitive to consumer demands and use pollution-prevention efforts to their utmost advantage by producing goods that are environmentally friendly.

5. *Federal and state grants.* Federal and state grant programs have been developed to strengthen pollution-prevention programs initiated by states and private entities. The EPA's "Pollution Prevention by and for Small Business" grant program awards grants to small businesses to assist their development and demonstration of new pollution-prevention technologies.

6. *Market incentives.* Public demand for environmentally preferred products has generated a market for recycled goods and related products; products can be designed with these environmental characteristics in mind, offering a competitive advantage. In addition, many private and public agencies are beginning to stimulate the market for recycled goods by writing contracts and specifications that call for the use of recycled materials.

7. *Reduced waste-treatment costs.* As discussed in reason no. 5 of the dirty dozen, the increasing costs of traditional end-of-pipe waste-management practices are avoided or reduced through the implementation of pollution-prevention programs.

8. *Potential tax incentives.* In an effort to promote pollution prevention, taxes may eventually need to be levied to encourage waste generators to consider reduction programs. Conversely, tax breaks could be developed for corporations that utilize pollution-prevention methods to foster pollution prevention.

9. *Decreased worker exposure.* By reducing or eliminating chemical exposures, businesses benefit by lessening the potential for chronic workplace exposure and serious accidents and emergencies. The burden of medical monitoring programs, personal exposure monitoring, and potential damage claims are also reduced.

10. *Decreased energy consumption.* As mentioned previously, methods of energy conservation are often interrelated and complementary to each other. Energy expenditures associated with the treatment and transport of waste are usually but not always reduced when the amount of waste generated is lessened, while at the same time the pollution associated with energy consumed by these activities is abated.

11. *Increased operating efficiencies.* A potential beneficial side effect of pollution-prevention activities is a concurrent increase in operating efficiency. Through a pollution-prevention assessment, the assessment team can identify sources of waste that result in hazardous waste generation *and* loss in process performance. The implementation of a reduction program will often rectify such problems through modernization, innovation, and the implementation of good operating practices.

12. *Competitive advantages.* By taking advantage of the many benefits associated with pollution prevention, businesses can gain a competitive edge.

13. *Reduced negative environmental impacts.* Through an evaluation of pollution-prevention alternatives, which consider a total systems approach, consideration is given to the negative impact of environmental damage to natural resources and species that occur during raw-material procurement and waste disposal. The performance of pollution-prevention endeavors will therefore result in enhanced environmental protection.

ECONOMIC CONSIDERATIONS ASSOCIATED WITH POLLUTION-PREVENTION PROGRAMS

The purpose of this subsection is to outline the basic elements of a pollution-prevention cost-accounting system that incorporates both traditional and less tangible economic variables. The intent is not to present a detailed discussion of economic analysis but to help identify the more important elements that must be considered to properly quantify pollution-prevention options.

The greatest driving force behind any pollution-prevention plan is the promise of economic opportunities and cost savings over the long term. Pollution prevention is now recognized as one of the lowest-cost options for waste/pollutant management. Hence, an understanding of the economics involved in pollution prevention programs/options is quite important in making decisions at both the engineering and management levels. Every engineer should be able to execute an economic evaluation of a proposed project. If the project cannot be justified economically after *all* factors—and these will be discussed in more detail below—have been taken into account, it should obviously not be pursued. The earlier such a project is identified, the fewer resources will be wasted.

Before the true cost or profit of a pollution-prevention program can be evaluated, the factors contributing to the economics must be recognized. There are two traditional contributing factors (capital costs and operating costs), but there are also other important costs and benefits associated with pollution prevention that need to be quantified if a meaningful economic analysis is going to be performed. Table 25-9 demonstrates the evolution of various cost-accounting methods. Although Tables 25-8 (see introduction) and 25-9 are not directly related, the reader is left with the option of comparing some of the similarities between the two.

The Total Systems Approach (TSA) referenced in Table 25-9 aims to quantify not only the economic aspects of pollution prevention but also the social costs associated with the production of a product or service from cradle to grave (i.e., life cycle). The TSA attempts to quantify less tangible benefits such as the reduced risk derived from not using a hazardous substance. The future is certain to see more emphasis placed on the TSA approach in any pollution-prevention program. As described earlier, a utility considering the option of converting from a gas-fired boiler to coal-firing is usually not concerned with the environmental effects and implications associated with such activities as mining, transporting, and storing the coal prior to its usage as an energy feedstock. Pollution-prevention approaches in the mid-to-late 1990s will become more aware of this need.

The economic evaluation referred to above is usually carried out using standard measures of profitability. Each company and organization has its own economic criteria for selecting projects for implementation. (For example, a project can be judged on its payback period. For some companies, if the payback period is more than 3 years, it is a dead issue.) In performing an economic evaluation, various costs and savings must be considered. The economic analysis presented in this subsection represents a preliminary, rather than a detailed, analysis. For smaller facilities with only a few (and perhaps simple) processes, the entire pollution-prevention assessment procedure will tend to be much less formal. In this situation, several obvious pollution-prevention options such as the installation of flow controls and good operating practices may be implemented with little

TABLE 25-9 Economic Analysis Timetable

Prior to 1945	Capital costs only
1945–1960	Capital and some operating costs
1960–1970	Capital and operating costs
1970–1975	Capital, operating, and some environmental control costs
1975–1980	Capital, operating, and environmental control costs
1980–1985	Capital, operating, and more sophisticated environmental control costs
1985–1990	Capital, operating, and environmental controls, and some life-cycle analysis (Total Systems Approach)
1990–1995	Capital, operating, and environmental control costs and life-cycle analysis (Total Systems Approach)
1995–2000	Widespread acceptance of Total Systems Approach
After 2000	???

or no economic evaluation. In these instances, no complicated analyses are necessary to demonstrate the advantages of adopting the selected pollution-prevention option. A proper perspective must also be maintained between the magnitude of savings that a potential option may offer and the amount of manpower required to do the technical and economic feasibility analyses. A short description of the various economic factors—including capital and operating costs and other considerations—follows.

Once identified, the costs and/or savings are placed into their appropriate categories and quantified for subsequent analysis. Equipment cost is a function of many variables, one of the most significant of which is capacity. Other important variables include operating temperature and/or pressure conditions, and degree of equipment sophistication. Preliminary estimates are often made using simple cost-capacity relationships that are valid when the other variables are confined to a narrow range of values.

The usual technique for determining the capital costs (i.e., total capital costs, which include equipment design, purchase, and installation) for the facility is based on the factored method of establishing direct and indirect installation costs as a function of the known equipment costs. This is basically a modified Lang method, whereby cost factors are applied to known equipment costs (Refs. 13 and 14). The first step is to obtain from vendors the purchase prices of the primary and auxiliary equipment. The total base price, designated by X, which should include instrumentation, control, taxes, freight costs, and so on, serves as the basis for estimating the direct and indirect installation costs. These costs are obtained by multiplying X by the cost factors, which are available in the literature (see Refs. 13–20).

The second step is to estimate the direct installation costs by summing all the cost factors involved in the direct installation costs, which include piping, insulation, foundation and supports, and so on. The sum of these factors is designated as the DCF (direct installation cost factor). The direct installation costs are then the product of the DCF and X. The third step consists of estimating the indirect installation costs; that is, all the cost factors for the indirect installation costs (engineering and supervision, startup, construction fees, and so on) are added; the sum is designated by ICF (indirect installation cost factor). The indirect installation costs are then the product of ICF and X. Once the direct and indirect installation costs have been calculated, the total capital cost (TCC) may be evaluated as follows:

$$\text{TCC} = X + (\text{DCF})(X) + (\text{ICF})(X)$$

This is then converted to annualized capital costs (ACC) with the use of the capital recovery factor (CRF), which can be calculated from the following equation:

$$\text{CRF} = \frac{(i)(1+i)^n}{(1+i)^n - 1}$$

where n = projected lifetime of the project, years
i = annual interest rate, expressed as a fraction

The annualized capital cost (ACC) is the product of the CRF and TCC and represents the total installed equipment cost distributed over the lifetime of the project. The ACC reflects the cost associated with the initial capital outlay over the depreciable life of the system. Although investment and operating costs can be accounted for in other ways such as present-worth analysis, the capital recovery method is preferred because of its simplicity and versatility. This is especially true when comparing somewhat similar systems having different depreciable lives. In such decisions, there are usually other considerations besides economic, but if all other factors are equal, the alternative with the lowest total annualized cost should be the most viable.

Operating costs can vary from site to site since these costs reflect local conditions (e.g., staffing practices, labor, utility costs). Operating costs, like capital costs, may be separated into two categories: direct and indirect costs. Direct costs are those that cover material and labor and are directly involved in operating the facility. These include labor, materials, maintenance and maintenance supplies, replacement parts, wastes, disposal fees, utilities, and laboratory costs. Indirect costs are those operating costs associated with, but not directly involved in, operating the facility; costs such as overhead (e.g., building/land leasing and office supplies), administrative fees, property taxes, and insurance fees) fall into this category. However, the major direct operating costs are usually those associated with labor and materials.

The main problem with the traditional type of economic analysis is that it is difficult—nay, in some cases impossible—to quantify some of the not-so-obvious economic merits of a pollution-prevention program. Several considerations have just recently surfaced as factors that need to be taken into account in any meaningful economic analysis of a pollution-prevention effort. What follows is a summary listing of these considerations, most which have been detailed earlier.

1. Decreased long-term liabilities
2. Regulatory compliance
3. Regulatory recordkeeping
4. Dealings with the EPA
5. Dealings with state and local regulatory bodies
6. Elimination or reduction of fines and penalties
7. Potential tax benefits
8. Customer relations
9. Stockholder support (corporate image)
10. Improved public image
11. Reduced technical support
12. Potential insurance costs and claims
13. Effect on borrowing power
14. Improved mental and physical well-being of employees
15. Reduced health-maintenance costs
16. Employee morale
17. Other process benefits
18. Improved worker safety
19. Avoidance of rising costs of waste treatment and/or disposal
20. Reduced training costs
22. Reduced emergency response planning

Many proposed pollution-prevention programs have been squelched in their early stages because a comprehensive economic analysis was not performed. Until the effects described above are included, the true merits of a pollution-prevention program may be clouded by incorrect and/or incomplete economic data. Can something be done by industry to remedy this problem? One approach is to use a modified version of the standard Delphi panel. In order to estimate these other economic benefits of pollution prevention, several knowledgeable individuals within and perhaps outside the organization are asked to independently provide estimates, with explanatory details, on these economic benefits. Each individual in the panel is then allowed to independently review all responses. The cycle is then repeated until the group's responses approach convergence.

Finally, pollution-prevention measures can provide a company with the opportunity of looking their neighbors in the eye and truthfully saying that all that can reasonably be done to prevent pollution is being done. In effect, the company is doing right by the environment. Is there an economic advantage to this? It is not only a difficult question to answer quantitatively but also a difficult one to answer qualitatively. The reader is left to ponder the answer to this question.

POLLUTION PREVENTION AT THE DOMESTIC AND OFFICE LEVELS

Concurrent with the United States' growth as an international economic superpower during the years following World War II, a new paradigm was established whereby society became accustomed to the convenience and ease with which goods could be discarded after a relatively short useful life. Individuals have come to expect these everyday comforts with what may be considered an unconscious ignorance towards the ultimate effect of the throwaway lifestyle. In fact, many, while fearful of environmental degradation, are not aware of the ill effect these actions have on the world as a whole. Many individuals who abide by the "not in my back yard" (NIMBY) mind-set also feel pollution prevention does not have to occur "in my house."

The past two decades have seen an increased social awareness of the impact of modern-day lifestyles on the environment. Public environmental concerns include issues such as waste disposal; hazardous-material regulations; depletion of natural resources; and air, water, and land pollution. Nevertheless, roughly one-half of the total quan-

tity of waste generated each year can be attributed to domestic sources!

More recently, concern about the environment has begun to stimulate environmentally correct behavior. After all, the choices made today affect the environment of tomorrow. Simple decisions can be made at work and at home that conserve natural resources and lessen the burden placed on a waste-management system. By eliminating waste at the source, society is participating in the protection of the environment by reducing the amount of waste that would otherwise need to be treated or ultimately disposed.

There are numerous areas of environmental concern that can be directly influenced by the consumer's actions. The first issue, which is described above, is that of waste generation. Second, energy conservation has significantly affected Americans and has resulted in cost-saving measures that have directly reduced pollution. As mentioned previously, energy conservation is directly related to pollution prevention since a reduction in energy use usually corresponds to less energy production and, consequently, less pollution output. A third area of concern is that of accident and emergency planning. Relatively recent accidents like Chernobyl and Bhopal have increased public awareness and helped stimulate regulatory policies concerned with emergency planning. Specifically, Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986 established the Emergency Planning and Community Right-to-Know Act and forever changed the concept of environmental management. This law attempts to avert potential emergencies through careful planning and the development of contingency plans. Planning for emergency situations can help protect human health and the environment (Ref. 21).

Based on the above three areas of potential concern, a plethora of waste reduction activities can be performed at home or in an office environment. One can easily note the similarities between these activities and those pollution-prevention activities performed in industry. The following few examples are identified by category according to this notation (Ref. 21):

- ● Waste reduction
- ★ Accidents, health, and safety
- ■ Energy conservation

At home

- ● Purchase products with the least amount of packaging
- ● Borrow items used infrequently
- ★ Handle materials to avoid spills (and slips, trips)
- ★ Keep hazardous materials out-of-reach of children
- ■ Use energy-efficient lighting (e.g., florescent)
- ■ Install water-flow restriction devices on sink faucets and showerheads

At the office

- ● Pass on verbal memos when written correspondence isn't required
- ● Reuse paper before recycling it
- ★ Know building evacuation procedures
- ★ Adhere to company medical policies (e.g., annual physicals)
- ■ Don't waste utilities simply because you are not paying for them
- ■ Take public transportation to the office

The use of pollution-prevention principles on the home front clearly does not involve the use of high-technology equipment or major lifestyle changes; success is only dependent upon active and willing public participation. All can help to make a difference.

Before pollution prevention becomes a fully accepted way of life, considerable effort still needs to be expended to change the way one looks at waste management. A desire to use "green" products and services will be of no avail in a market where these goods are not available. Participation in pollution-prevention programs will increase through continued education, community efforts, and lobbying for change. Market incentives can be created and strengthened by tax policies, price preferences, and packaging regulations created at the federal, state, and local levels. Each individual should take part by communicating with industry and expressing concerns. For example, citizens should feel free to write letters to decision makers at both business organizations and government institutions regarding specific products or legislation. Letters can be positive, demonstrating personal endorsement of a green product, or disapproving, expressing discontent and reluctance to use a particular product because of its negative environmental effect (Ref. 21).

By starting now, society will learn through experience to better manage its waste while providing a safer and cleaner environment for future generations.

ETHICAL CONSIDERATIONS

Given the evolutionary nature of pollution prevention, it is evident that as technology changes and continued progress is achieved, society's opinion of both what is possible and desirable will also change. Government officials, scientists, and engineers will face new challenges to fulfill society's needs while concurrently meeting the requirements of changing environmental regulations. It is now apparent that attention should also be given to ethical considerations and their application to pollution prevention policy. How one makes decisions on the basis of ethical beliefs is clearly a personal issue but one that should be addressed. In order to examine this issue, the meaning of ethics must be known, although the intent here is not to provide a detailed discussion regarding the philosophy of ethics or morality.

Ethics can simply be defined as the analysis of the rightness and wrongness of an act or actions. According to Dr. Andrew Varga, director of the Philosophical Resources Program at Fordham University, in order to discern the morality of an act, it is customary to look at the act on the basis of four separate elements: its object, motive, circumstances, and consequences (Ref. 22). Rooted in this analysis is the belief that if one part of the act is bad, then the overall act itself cannot be considered good. Of course, there are instances where the good effects outweigh the bad, and therefore there may be a reason to permit the evil. The application of this principle is not cut and dry and requires decisions to be made on a case-by-case basis. Each must make well-judged decisions rooted in an understanding of the interaction between technology and the environment. After all, the decisions made today will have an impact not only on this generation but on many generations to come. If one chooses today not to implement a waste-reduction program in order to meet a short-term goal of increased productivity, this might be considered a good decision since it benefits the company and its employees. However, should a major release occur that results in the contamination of a local sole-source of drinking water, what is the good?

As an additional example, toxicological studies have indicated that test animals exposed to small quantities of toxic chemicals had better health than control groups that were not exposed. A theory has been developed that says that a low-level exposure to the toxic chemical results in a challenge to the animal to maintain homeostasis; this challenge increases the animal's vigor and, correspondingly, its health. However, larger doses seem to cause an inability to adjust, resulting in negative health effects. Based on this theory, some individuals would believe that absolute pollution reduction might not be necessary.

FUTURE TRENDS

The reader should keep an open mind when dealing with the types of issues discussed above and facing challenges perhaps not yet imagined. Clearly, there is no simple solution or answer to many of the questions. The EPA is currently *attempting* to develop a partnership with government, industry, and educators to produce and distribute pollution-prevention educational materials. Given EPA's past history and performance, there are understandable doubts as to whether this program will succeed (Ref. 23).

Finally, no discussion on pollution prevention would be complete without reference to the activities of the 49-year-old International Organization for Standardization (ISO). ISO recently created Technical Committee 207 (TC 207) to begin work on new standards for environmental management systems (EMS). The ramifications, especially to the chemical industry, which has become heavily involved in the development of these standards, will be great. TC 207's activities are

being scrutinized closely and will continue to be into 1997 when the first environmental standards are expected to be published. This new environmental management set of standards will be entitled ISO 14000. Once this new standard is in place, it is expected that customers will require their product suppliers to be certified by ISO 14000. In addition, some service suppliers who have an impact on the environment will also probably be expected to obtain an ISO 14000 certification. Certification will imply to the customer that, when the product or service was prepared, the environment was not significantly damaged in the process. This will effectively require that the life-cycle design mentality discussed earlier be applied to all processes. Implementing the life-cycle design framework will require significant organizational and operational changes in business. To effectively promote the goals of sustainable development, life-cycle designs will have to successfully address cost, performance, and cultural and legal factors.

The impact of all of the above on both the industry and the consumer will be significant. All have heard the expression "I've met the enemy . . . and we're it." After all, it is the consumer who can and will ultimately have the final say. Once the consumer refuses to buy and/or accept products and/or services that damage the environment, that industry is either out of business or must change its operations to environmentally acceptable alternatives. With the new standards, customers (in addition to other organizations) of certified organizations will be assured that the products or services they purchase have been produced in accordance with universally accepted standards of environmental management. Organizational claims, which today can be misleading or erroneous, will, under the standards, be backed up by comprehensive and detailed environmental management systems that must withstand the scrutiny of intense audits.

Can all of the above be achieved in the near future? If it can, then society need only key its environmental efforts on educating the consumer.

AIR-POLLUTION MANAGEMENT OF STATIONARY SOURCES

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INTRODUCTION

Air pollutants may be classified into two broad categories: (1) natural and (2) human-made. Natural sources of air pollutants include:

- Windblown dust
- Volcanic ash and gases
- Ozone from lightning and the ozone layer
- Esters and terpenes from vegetation
- Smoke, gases, and fly ash from forest fires
- Pollens and other aeroallergens
- Gases and odors from biologic activities
- Natural radioactivity

Such sources constitute background pollution and that portion of the pollution problem over which control activities can have little, if any, effect.

Human-made sources cover a wide spectrum of chemical and physical activities and are the major contributors to urban air pollution. Air pollutants in the United States pour out from over 10 million vehicles, the refuse of over 250 million people, the generation of billions of kilowatts of electricity, and the production of innumerable products demanded by everyday living. Hundreds of millions of tons of air pollutants are generated annually in the United States alone. The five main classes of pollutants are particulates, sulfur dioxide, nitrogen oxides, volatile organic compounds, and carbon monoxide. Total emissions in the United States are summarized by source category for the year 1993 in Table 25-10.

Air pollutants may also be classified as to the origin and state of matter:

1. Origin
   a. Primary. Emitted to the atmosphere from a process
   b. Secondary. Formed in the atmosphere as a result of a chemical reaction
2. State of matter
   a. Gaseous. True gases such as sulfur dioxide, nitrogen oxide, ozone, carbon monoxide, etc.; vapors such as gasoline, paint solvent, dry cleaning agents, etc.
   b. Particulate. Finely divided solids or liquids; solids such as dust, fumes, and smokes; and liquids such as droplets, mists, fogs, and aerosols

Gaseous Pollutants Gaseous pollutants may be classified as inorganic or organic. Inorganic pollutants consist of:

1. *Sulfur gases.* Sulfur dioxide, sulfur trioxide, hydrogen sulfide
2. *Oxides of carbon.* Carbon monoxide, carbon dioxide
3. *Nitrogen gases.* Nitrous oxide, nitric oxide, nitrogen dioxide, other nitrous oxides
4. *Halogens, halides.* Hydrogen fluoride, hydrogen chloride, chlorine, fluorine, silicon tetrafluoride
5. *Photochemical products.* Ozone, oxidants
6. *Cyanides.* Hydrogen cyanide
7. *Ammonium compounds.* Ammonia
8. *Chlorofluorocarbons.* 1,1,1-trichloro-2,2,2-trifluoroethane; trichlorofluoromethane, dichlorodifluoromethane; chlorodifluoromethane; 1,2-dichloro-1,1,2,2-tetrafluoroethane; chloropentafluoroethane

Organic pollutants consist of:

1. Hydrocarbons
   a. Paraffins. Methane, ethane, octane
   b. Acetylene
   c. Olefins. Ethylene, butadiene
   d. Aromatics. Benzene, toluene, benzpyrene, xylene, styrene
2. Aliphatic oxygenated compounds
   a. Aldehydes. Formaldehyde
   b. Ketones. Acetone, methylethylketone

TABLE 25-10 1993 National Emissions by Source Category in short tons ×1000

Source category	Particulate (PM-10)	Sulfur dioxide	Nitrogen oxides	Volatile organic compounds	Carbon monoxide
Fuel combustion					
Electric utility	270	15836	7782	36	322
Industrial	219	2830	3176	271	667
Other	723	600	732	341	4444
Chemical and allied product manufacturing	75	450	414	1811	1998
Metals processing	141	580	82	74	2091
Petroleum and related industries	26	409	95	720	398
Other industrial processes	311	413	314	486	732
Solvent utilization	2	1	3	6249	2
Storage and transport	55	5	3	1861	56
Waste disposal and recycling	248	37	84	2271	1732
Highway vehicles	197	438	7437	6094	59989
Off-highway	395	278	2986	2207	15272
Natural sources—wind erosion	628				
Miscellaneous	42200	11	296	893	9506
Fugitive dust	41801				
Nonfugitive dust	399				
Total	45490	21888	23404	23314	97209

SOURCE: EPA-454/R-94-027, National Air Pollutant Emission Trends, 1900–1993.

c. Organic acids
d. Alcohols. Methanol, ethanol, isopropanol
e. Organic halides. Cyanogen chloride bromobenzyl cyanide
f. Organic sulfides. Dimethyl sulfide
g. Organic hydroperoxides. Peroxyacetyl nitrite or nitrate (PAN)

The most common gaseous pollutants and their major sources and significance are presented in Table 25-11.

Particulate Pollutants Particulates may be defined as solid or liquid matter whose effective diameter is larger than a molecule but smaller than approximately 100 μm. Particulates dispersed in a gaseous medium are collectively termed an *aerosol.* The terms *smoke, fog, haze,* and *dust* are commonly used to describe particular types of aerosols, depending on the size, shape, and characteristic behavior of the dispersed particles. Aerosols are rather difficult to classify on a scientific basis in terms of their fundamental properties such as settling rate under the influence of external forces, optical activity, ability to absorb an electrical charge, particle size and structure, surface-to-volume ratio, reaction activity, physiological action, and so on. In general, particle size and settling rate have been the most characteristic properties for many purposes. On the other hand, particles on the order of 1 μm or less settle so slowly that, for all practical purposes, they are regarded as permanent suspensions. Despite possible advantages of scientific classification schemes, the use of popular descriptive terms such as smoke, dust, and mist, which are essentially based on the mode of formation, appears to be a satisfactory and convenient method of classification. In addition, this approach is so well established and understood that it undoubtedly would be difficult to change.

Dust is typically formed by the pulverization or mechanical disintegration of solid matter into particles of smaller size by processes such as grinding, crushing, and drilling. Particle sizes of dust range from a lower limit of about 1 μm up to about 100 or 200 μm and larger. Dust particles are usually irregular in shape, and particle size refers to some average dimension for any given particle. Common examples include fly ash, rock dusts, and ordinary flour. *Smoke* implies a certain degree of optical density and is typically derived from the burning of organic materials such as wood, coal, and tobacco. Smoke particles are very fine, ranging in size from less than 0.01 μm up to 1 μm. They are usually spherical in shape if of liquid or tarry composition and irregular in shape if of solid composition. Owing to their very fine particle size, smokes can remain in suspension for long periods of time and exhibit lively brownian motion.

Fumes are typically formed by processes such as sublimation, condensation, or combustion, generally at relatively high temperatures. They range in particle size from less than 0.1 μm to 1 μm. Similar to smokes, they settle very slowly and exhibit strong brownian motion.

Mists or fogs are typically formed either by the condensation of water or other vapors on suitable nuclei, giving a suspension of small liquid droplets, or by the atomization of liquids. Particle sizes of natural fogs and mists lie between 2 and 200 μm. Droplets larger than 200 μm are more properly classified as drizzle or rain. Many of the important properties of aerosols that depend on particle size are presented in Sec. 17, Fig. 17-34.

When a liquid or solid substance is emitted to the air as particulate matter, its properties and effects may be changed. As a substance is broken up into smaller and smaller particles, more of its surface area is exposed to the air. Under these circumstances, the substance, whatever its chemical composition, tends to combine physically or chemically with other particles or gases in the atmosphere. The resulting combinations are frequently unpredictable. Very small aerosol particles (from 0.001 to 0.1 μm) can act as condensation nuclei to facilitate the condensation of water vapor, thus promoting the formation of fog and ground mist. Particles less than 2 or 3 μm in size (about half by weight of the particles suspended in urban air) can penetrate the mucous membrane and attract and convey harmful chemicals such as sulfur dioxide. In order to address the special concerns related to the effects of very fine, inhalable particulates, EPA replaced its ambient air standards for total suspended particulates (TSP) with standards for particlute matter less than 10 μm in size (PM_{10}).

By virtue of the increased surface area of the small aerosol particles and as a result of the adsorption of gas molecules or other such properties that are able to facilitate chemical reactions, aerosols tend to exhibit greatly enhanced surface activity. Many substances that oxidize slowly in their massive state will oxidize extremely fast or possibly even explode when dispersed as fine particles in the air. Dust explosions, for example, are often caused by the unstable burning or oxidation of combustible particles, brought about by their relatively large specific surfaces. Adsorption and catalytic phenomena can also be extremely important in analyzing and understanding the problems of particulate pollution. The conversion of sulfur dioxide to corrosive sulfuric acid assisted by the catalytic action of iron oxide particles, for example, demonstrates the catalytic nature of certain types of particles in the atmosphere. Finally, aerosols can absorb radiant energy and rapidly conduct heat to the surrounding gases of the atmosphere. These are gases that ordinarily would be incapable of absorbing radiant energy by themselves. As a result, the air in contact with the aerosols can become much warmer.

Estimating Emissions from Sources Knowledge of the types and rates of emissions is fundamental to evaluation of any air pollution problem. A comprehensive material balance on the process can often assist in this assessment. Estimates of the rates at which pollutants are discharged from various processes can also be obtained by utilizing published emission factors. See *Compilation of Air Pollution Emission Factors (AP-42),* 4th ed., U.S. EPA, Research Triangle Park, North Carolina, September, 1985, with all succeeding supplements and the EPA Technology Transfer Network's CHIEF. The emission factor is a statistical average of the rate at which pollutants are emitted from the

TABLE 25-11 Typical Gaseous Pollutants and Their Principal Sources and Significance

Air pollutants	From manufacturing sources such as these	In typical industries	Cause these damaging effects
Alcohols	Used as a solvent in coatings	Surface coatings, printing	Sensory and respiratory irritation
Aldehydes	Results from thermal decomposition of fats, oil, or glycerol; used in some glues and binders	Food processing, light process, wood furniture, chip board	An irritating odor, suffocating, pungent, choking; not immediately dangerous to life; can become intolerable in a very short time
Ammonia	Used in refrigeration, chemical processes such as dye making, explosives, lacquer, fertilizer	Textiles, chemicals	Corrosive to copper, brass, aluminum, and zinc; high concentration producing chemical burns on wet skin
Aromatics	Used as a solvent in coatings	Surface coatings, printing	Irritation of mucous membranes, narcotic effects; some are carcinogens
Arsine	Any soldering, pickling, etching, or plating process involving metals or acids containing arsenic	Chemical processing, smelting	Breakdown of red cells in blood
Carbon dioxide	Fuel combustion; calcining	Industrial boilers, cement and lime production	Greenhouse gas
Carbon monoxide	Fuming of metallic oxides, gas-operated fork trucks	Primary metals; steel and aluminum	Reduction in oxygen-carrying capacity of blood
Chlorine	Manufactured by electrolysis, bleaching cotton and flour; by-product of organic chemicals	Textiles, chemicals	Attacks entire respiratory tract and mucous membrane of eye
Chlorofluorocarbons	Used in refrigeration and production of porous foams; degreasing agent	Refrigeration, plastic foam production, metal fabricating	Attacks stratospheric ozone layer; greenhouse gas
Hydrochloric acid	Combustion of coal or wastes containing chlorinated plastics	Coal-fired boilers, incinerators	Irritant to eyes and respiratory system
Hydrogen cyanide	From metal plating, blast furnaces, dyestuff works	Metal fabricating, primary metals, textiles	Capable of affecting nerve cells
Hydrogen fluoride	Catalyst in some petroleum refining, etching glass, silicate extraction; by-product in electrolytic production of aluminum	Petroleum, primary metals, aluminum	Strong irritant and corrosive action on all body tissue; damage to citrus plants, effect on teeth and bones of cattle from eating plants
Hydrogen sulfide	Refinery gases, crude oil, sulfur recovery, various chemical industries using sulfur compounds	Petroleum and chemicals; Kraft pulping process	Foul odor of rotten eggs; irritating to eyes and respiratory tract; darkening exterior paint
Ketones	Used as a solvent in coatings	Surface coatings, printing	Sensory and respiratory irritation
Lead	Incineration, smelting and casting, transportation.	Copper and lead smelting, MSWs	Neurological impairments; kidney, liver, and heart damage.
Nitrogen oxides	High-temperature combustion: metal cleaning, fertilizer, explosives, nitric acid; carbon-arc combustion; manufacture of H_2SO_4	Metal fabrication, heavy chemicals	Irritating gas affecting lungs; vegetation damage
Odors	Slaughtering and rendering animals, tanning animal hides, canning, smoking meats, roasting coffee, brewing beer, processing toiletries	Food processing, allied industries	Objectionable odors
Ozone	Reaction product of VOC and nitrogen oxides	Not produced directly	Irritant to eyes and respiratory system
Phosgenes	Thermal decomposition of chlorinated hydrocarbons, degreasing, manufacture of dyestuffs, pharmaceuticals, organic chemicals	Metal fabrication, heavy chemicals	Damage capable of leading to pulmonary edema, often delayed
Sulfur dioxide	Fuel combustion (coal, oil), smelting and casting, manufacture of paper by sulfite process	Primary metals (ferrous and nonferrous); pulp and paper	Sensory and respiratory irritation, vegetation damage, corrosion, possible adverse effect on health

burning or processing of a given quantity of material or on the basis of some other meaningful parameter. Emission factors are affected by the techniques employed in the processing, handling, or burning operations, by the quality of the material used, and by the efficiency of the air-pollution control. Since the combination of these factors tends to be unique to a source, emission factors appropriate for one source may not be satisfactory for another source. Hence, care and good judgment must be exercised in identifying appropriate emission factors. If appropriate emission factors cannot be found or if air-pollution control equipment is to be designed, specific source sampling should be conducted. The major industrial sources of pollutants, the air contaminants emitted, and typical control techniques are summarized in Table 25-12.

Effects of Air Pollutants

Materials The damage that air pollutants can do to some materials is well known: ozone in photochemical smog cracks rubber, weakens fabrics, and fades dyes; hydrogen sulfide tarnishes silver; smoke dirties laundry; acid aerosols ruin nylon hose. Among the most important effects are discoloration, corrosion, the soiling of goods, and impairment of visibility.

TABLE 25-12 Control Techniques Applicable to Unit Processes at Important Emission Sources

Industry	Process of operation	Air contaminants emitted	Control techniques
Aluminum reduction plants	Materials handling: Buckets and belt Conveyor or pneumatic conveyor	Particulates (dust)	Exhaust systems and baghouse
	Anode and cathode electrode preparation:		Exhaust systems and mechanical collectors
	Cathode (baking)	Hydrocarbon emissions from binder	
	Anode (grinding and blending)	Particulates (dust)	
	Baking	Particulates (dust), CO, SO_2, hydrocarbons, and fluorides	High-efficiency cyclone, electrostatic precipitators, scrubbers, catalytic combustion or incinerators, flares, baghouse
	Pot charging	Particulates (dust), CO, HF, SO_2, CF_4, and hydrocarbons	High-efficiency cyclone, baghouse, spray towers, floating-bed scrubber, electrostatic precipitators, chemisorption, wet electrostatic precipitators
	Metal casting	Cl_2, HCl, CO, and particulates (dust)	Exhaust systems and scrubbers
Asphalt plants	Materials handling, storage and classifiers: elevators, chutes, vibrating screens	Particulates (dust)	Wetting; exhaust systems with a scrubber or baghouse
	Drying: rotary oil- or gas-fired	Particulates, SO_2, NO_x, VOC, CO, and smoke	Proper combustion controls, fuel-oil preheating where required; local exhaust system, cyclone and a scrubber or baghouse
	Truck traffic	Dust	Paving, wetting down truck routes
Cement plants	Quarrying: primary crusher, secondary crusher, conveying, storage	Particulates (dust)	Wetting; exhaust systems with fabric filters
	Dry processes: materials handling, air separator (hot-air furnace)	Particulates (dust)	Local exhaust system with mechanical collectors and baghouse
	Grinding	Particulates (dust)	Local exhaust system with cyclones and baghouse
	Pneumatic, conveying and storage	Particulates (dust)	
	Wet process: materials handling, grinding, storage	Wet materials, no dust	
	Kiln operations: rotary kiln	Particulates (dust), CO, SO_x, NO_x, hydrocarbons, aldehydes, ketones	Electrostatic precipitators, acoustic horns and baghouses, scrubber
	Clinker cooling: materials handling	Particulates (dust)	Local exhaust system and electrostatic precipitators or fabric filters
	Grinding and packing, air separator, grinding, pneumatic conveying, materials handling, packaging	Particulates (dust)	Local exhaust system and fabric filters
Coal-preparation plants	Materials handling: conveyors, elevators, chutes	Particulates (dust)	Local exhaust system and cyclones
	Sizing: crushing, screening, classifying	Particulates (dust)	Local exhaust system and cyclones
	Dedusting	Particulates (dust)	Local exhaust system, cyclone precleaners, and baghouse
	Storing coal in piles	Blowing particulates (dust)	Wetting, plastic-spray covering
	Refuse piles	H_2S, particulates, and smoke from burning storage piles	Digging out fire, pumping water onto fire area, blanketing with incombustible material
	Coal drying: rotary, screen, suspension, fluid-bed, cascade	Dust, smoke, particulates, sulfur oxides, H_2S	Exhaust systems with cyclones and fabric filters
Coke plants	By-product-ovens charging	Smoke, particulates (dust)	Pipe-line charging, careful charging techniques, portable hooding and scrubber or baghouses
	Pushing	Smoke, particulates (dust), SO_2	Minimizing green-coke pushing, scrubbers and baghouses
	Quenching	Smoke, particulates (dust and mists), phenols, and ammonia	Baffles and spray tower
	By-product processing	CO, H_2S, methane, ammonia, H_2, phenols, hydrogen cyanide, N_2, benzene, xylene, etc.	Electrostatic precipitator, scrubber, flaring
	Material storage (coal and coke)	Particulates (dust)	Wetting, plastic spray, fire-prevention techniques
Fertilizer industry (chemical)	Phosphate fertilizers: crushing, grinding, and calcining	Particulates (dust)	Exhaust system, scrubber, cyclone, baghouse
	Hydrolysis of P_2O_5	PH_3, $P_2O_5PO_4$ mist	Scrubbers, flare
	Acidulation and curing	HF, SiF_4	Scrubbers
	Granulation	Particulates (dust)(product recovery)	Exhaust system, scrubber, or baghouse
	Ammoniation	NH_3, NH_4Cl, SiF_4, HF	Cyclone, electrostatic precipitator, baghouse, high-energy scrubber
	Nitric acid acidulation	NO_x, gaseous fluoride compounds	Scrubber, addition of urea
	Superphosphate storage and shipping	Particulates (dust)	Exhaust system, cyclone or baghouse
	Ammonium nitrate reactor	NH_3, NO_x	Scrubber
	Prilling tower	NH_4, NO_3	Proper operation control, scrubbers

TABLE 25-12 Control Techniques Applicable to Unit Processes at Important Emission Sources (*Continued*)

Industry	Process of operation	Air contaminants emitted	Control techniques
Foundries:	Melting (cupola:)		
Iron	Charging	Smoke and particulates	Closed top with exhaust system, CO afterburner, gas-cooling device and scrubbers, baghouse or electrostatic precipitator, wetting to extinguish fire
	Melting	Smoke and particulates, fume	
	Pouring	Oil, mist, CO	
	Bottom drop	Smoke and particulates	
Brass and bronze	Melting:		
	Charging	Smoke particulates, oil mist	Low-zinc-content red brass: use of good combustion controls and slag cover; high-zinc-content brass: use of good combustion controls, local exhaust system, and baghouse or scrubber
	Melting	Zinc oxide fume, particulates, smoke	
	Pouring	Zinc oxide fume, lead oxide fume	
Aluminum	Melting: charging, melting, pouring	Smoke and particulates	Charging clean material (no paint or grease); proper operation required; no air-pollution-control equipment if no fluxes are used and degassing is not required; dirty charge requiring exhaust system with scrubbers and baghouses
Zinc	Melting:		
	Charging	Smoke and particulates	Exhaust system with cyclone and baghouse, charging clean material (no paint or grease)
	Melting	Zinc oxide fume	Careful skimming of dross
	Pouring	Oil mist and hydrocarbons from diecasting machines	Use of low-smoking die-casting lubricants
	Sand-handling shakeout	Particulates (dust), smoke, organic vapors	
	Magnetic pulley, conveyors, and elevators, rotary cooler, screening, crusher-mixer	Particulates (dust)	Exhaust system, cyclone, and baghouse
	Coke-making ovens	Organic acids, aldehydes, smoke, hydrocarbons	Use of binders that will allow ovens to operate at less than 204°C (400°F) or exhaust systems and afterburners
Galvanizing operations	Hot-dip-galvanizing-tank kettle: dipping material into the molten zinc; dusting flux onto the surface of the molten zinc	Fumes, particulates (liquid), vapors: NH_4Cl, ZnO, $ZnCl_2$, Zn, NH_3, oil, and carbon	Close-fitting hoods with high in-draft velocities (in some cases, the hood may not be able to be close to the kettle, so the in-draft velocity must be very high), baghouses, electrostatic precipitators
Kraft pulp mills	Digesters: batch and continuous	Mercaptans, methanol (odors)	Condensers and use of lime kiln, boiler, or furnaces as afterburners
	Multiple-effect evaporators	H_2S, other odors	Caustic scrubbing and thermal oxidation of noncondensables
	Recovery furnace	H_2S, mercaptans, organic sulfides, and disulfides	Proper combustion controls for fluctuating load and unrestricted primary and secondary air flow to furnace and dry-bottom electrostatic precipitator; noncontact evaporator
	Weak and strong black-liquor oxidation	H_2S	Packed tower and cyclone
	Smelt tanks	Particulates (mist or dust)	Demisters, venturi, packed tower, or impingement-type scrubbers
	Lime kiln	Particulates (dust), H_2S	Venturi scrubbers
Municipal and industrial incinerators	Single-chamber incinerators	Particulates, smoke, volatiles, CO, SO_x, ammonia, organic acids, aldehydes, NO_x, dioxins hydrocarbons, odors, HCl, furans	Afterburner, combustion controls
	Multiple-chamber incinerators (retort, inline):	Particulates, smoke, and combustion contaminants	Operating at rated capacity, using auxiliary fuel as specified, and good maintenance, including timely cleanout of ash
	Flue-fed	Particulates, smoke, and combustion contaminants	Use of charging gates and automatic controls for draft; afterburner
	Wood waste	Particulates, smoke, and combustion contaminants	Continuous-feed systems; operation at design load and excess air; cyclones
	Municipal incinerators (50 tons and up per day):	Particulates, smoke, volatiles, CO, ammonia, organic acids, aldehydes, NO_x, furans, hydrocarbons, SO_x, hydrogen chloride, dioxins and odors	Preparation of materials, including weighing, grinding, shredding; control of tipping area, furnace design with proper automatic controls; proper start-up techniques; maintenance of design operating temperatures; use of electrostatic precipitators, scrubbers, and baghouses; proper ash cleanout

TABLE 25-12 Control Techniques Applicable to Unit Processes at Important Emission Sources (*Continued*)

Industry	Process of operation	Air contaminants emitted	Control techniques
Municipal and industrial incinerators	Pathological incinerators	Odors, hydrocarbons, HCl, dioxins, furans	Proper charging, acid gas scrubber, baghouse
	Industrial waste	Particulates, smoke, and combustion contaminants	Modified fuel feed, auxiliary fuel and dryer systems, cyclones, scrubbers
Nonferrous smelters, primary:			
Copper	Roasting	SO_2, particulates, fume	Exhaust system, settling chambers, cyclones or scrubbers and electrostatic precipitators for dust and fumes and sulfuric acid plant for SO_2
	Reverberatory furnace	Smoke, particulates, metal oxide fumes, SO_2	Exhaust system, settling chambers, cyclones or scrubbers and electrostatic precipitators for dust and fumes and sulfuric acid plant for SO_2
	Converters: charging, slag skim, pouring, air or oxygen blow	Smoke, fume, SO_2	Exhaust system, settling chambers, cyclones or scrubbers and electrostatic precipitators for dust and fumes and sulfuric acid plant for SO_2
Lead	Sintering	SO_2, particulates, smoke	Exhaust system, cyclones and baghouse or precipitators for dust and fumes, sulfuric acid plant for SO_2
	Blast furnace	SO_2, CO, particulates, lead oxide, zinc oxide	Exhaust system, settling chambers, afterburner and cooling device, cyclone, and baghouse
	Dross reverberatory furnace	SO_2, particulates, fume	Exhaust system, settling chambers, cyclone and cooling device, baghouse
	Refining kettles	SO_2, particulates	Local exhaust system, cooling device, baghouse or precipitator
Cadmium	Roasters, slag, fuming furnaces, deleading kilns	Particulates	Local exhaust system, baghouse or precipitator
Zinc	Roasting	Particulates (dust) and SO_2	Exhaust system, humidifier, cyclone, scrubber, electrostatic precipitator, and acid plant
	Sintering	Particulates (dust) and SO_2	Exhaust system, humidifier, electrostatic precipitator, and acid plant
	Calcining	Zinc oxide fume, particulates, SO_2, CO	Exhaust system, baghouse, scrubber or acid plant
	Retorts: electric arc		
Nonferrous smelters, secondary	Blast furnaces and cupolas-recovery of metal from scrap and slag	Dust, fumes, particulates, oil vapor, smoke, CO	Exhaust systems, cooling devices, CO burners and baghouses or precipitators
	Reverberatory furnaces	Dust, fumes, particulates, smoke, gaseous fluxing materials	Exhaust systems, and baghouses or precipitators, or venturi scrubbers
	Sweat furnaces	Smoke, particulates, fumes	Precleaning metal and exhaust systems with afterburner and baghouse
	Wire reclamation and autobody burning	Smoke, particulates	Scrubbers and afterburners
Paint and varnish manufacturing	Resin manufacturing: closed reaction vessel	Acrolein, other aldehydes and fatty acids (odors), phthalic anhydride (sublimed)	Exhaust systems with scrubbers and fume burners
	Varnish: cooking-open or closed vessels	Ketones, fatty acids, formic acids, acetic acid, glycerine, acrolein, other aldehydes, phenols and terpenes; from tall oils, hydrogen sulfide, alkyl sulfide, butyl mercaptan, and thiofen (odors)	Exhaust system with scrubbers and fume burners; close-fitting hoods required for open kettles
	Solvent thinning	Olefins, branched-chain aromatics and ketones (odors), solvents	Exhaust system with fume burners
Rendering plants	Feedstock storage and housekeeping	Odors	Quick processing, washdown of all concrete surfaces, paving of dirt roads, proper sewer maintenance, enclosure, packed towers
	Cookers and percolators	SO_2, mercaptans, ammonia, odors	Exhaust system, condenser, scrubber, or incinerator
	Grinding	Particulates (dust)	Exhaust system and scrubber
Roofing plants (asphalt saturators)	Felt or paper saturators: spray section, asphalt tank, wet looper	Asphalt vapors and particulates (liquid)	Exhaust system with high inlet velocity at hoods (3658 m/s [>200 ft/min]) with either scrubbers, baghouses, or two-stage low-voltage electrostatic precipitators
	Crushed rock or other minerals handling	Particulates (dust)	Local exhaust system, cyclone or multiple cyclones

TABLE 25-12 Control Techniques Applicable to Unit Processes at Important Emission Sources (*Concluded*)

Industry	Process of operation	Air contaminants emitted	Control techniques
Steel mills	Blast furnaces: charging, pouring	CO, fumes, smoke, particulates (dust)	Good maintenance, seal leaks; use of higher ratio of pelletized or sintered ore; CO burned in waste-heat boilers, stoves, or coke ovens; cyclone, scrubber, and baghouse
	Electric steel furnaces: charging, pouring, oxygen blow	Fumes, smoke, particulates (dust), CO	Segregating dirty scrap; proper hooding, baghouses or electrostatic precipitator
	Open-hearth furnaces: oxygen blow, pouring	Fumes, smoke, SO_x, particulates (dust), CO, NO_x	Proper hooding, settling chambers, waste-heat boiler, baghouse, electrostatic precipitator, and wet scrubber
	Basic oxygen furnaces: oxygen blowing	Fumes, smoke, CO, particulates (dust)	Proper hooding (capturing of emissions and dilute CO), scrubbers, or electrostatic precipitator
	Raw material storage	Particulates (dust)	Wetting or application of plastic spray
	Pelletizing	Particulates (dust)	Proper hooding, cyclone, baghouse
	Sintering	Smoke, particulates (dust), SO_2, NO_x	Proper hooding, cyclones, wet scrubbers, baghouse, or precipitator

1. *Discoloration.* Many air pollutants accumulate on and discolor buildings. Not only does sooty material blacken buildings, but it can accumulate and become encrusted. This can hide lines and decorations and thereby disfigure structures and reduce their aesthetic appeal. Another common effect is the discoloration of paint by certain acid gases. A good example is the blackening of white paint with a lead base by hydrogen sulfide.

2. *Corrosion.* A more serious effect and one of great economic importance is the corrosive action of acid gases on building materials. Such acids can cause stone surfaces to blister and peel; mortar can be reduced to powder. Metals are also damaged by the corrosive action of some pollutants. Another common effect is the deterioration of tires and other rubber goods. Cracking and apparent "drying" occur when these goods are exposed to ozone and other oxidants.

3. *Soiling of goods.* Clothes, real estate, automobiles, and household goods can easily be soiled by air contaminants, and the more frequent cleaning thus required can become expensive. Also, more frequent cleaning often leads to a shorter life span for materials and to the need to purchase goods more often.

4. *Impairment of visibility.* The impairment of atmospheric visibility (i.e., decreased visual range through a polluted atmosphere) is caused by the scattering of sunlight by particles suspended in the air. It is not a result of sunlight being obscured by materials in the air. Since light scattering, and not obscuration, is the main cause of the reduction in visibility, reduced visibility due to the presence of air pollutants occurs primarily on bright days. On cloudy days or at night there may be no noticeable effect, although the same particulate concentration may exist at these times as on sunny days. Reduction in visibility creates several problems. The most significant are the adverse effects on aircraft, highway, and harbor operations. Reduced visibility can reduce quality of life and also cause adverse aesthetic impressions that can seriously affect tourism and restrict the growth and development of any area. Extreme conditions such as dust storms or sandstorms can actually cause physical damage by themselves.

Vegetation Vegetation is more sensitive than animals to many air contaminants, and methods have been developed that use plant response to measure and identify contaminants. The effects of air pollution on vegetation can appear as death, stunted growth, reduced crop yield, and degradation of color. It is interesting to note that in some cases of color damage such as the silvering of leafy vegetables by oxidants, the plant may still be used as food without any danger to the consumer; however, the consumer usually will not buy such vegetables on aesthetic grounds, so the grower still sustains a loss. Among the pollutants that can harm plants are sulfur dioxide, hydrogen fluoride, and ethylene. Plant damage caused by constituents of photochemical smog has been studied extensively. Damage has been attributed to ozone and peroxyacetyl nitrites, higher aldehydes, and products of the reaction of ozone with olefins. However, none of the cases precisely duplicates all features of the damage observed in the field, and the question remains open to some debate and further study.

Animals Considerable work continues to be performed on the effects of pollutants on animals, including, for a few species, experiments involving mixed pollutants and mixed gas-aerosol systems. In general, such work has shown that mixed pollutants may act in several different ways. They may produce an effect that is additive, amounting to the sum of the effects of each contaminant acting alone; they may produce an effect that is greater than the simply additive (synergistic) or less than the simply additive (antagonistic); or they may produce an effect that differs in some other way from the simply additive.

The mechanism by which an animal can become poisoned in many instances is completely different from that by which humans are affected. As in humans, inhalation is an important route of entry in acute air-pollution exposures such as the Meuse Valley and Donora incidents (see the paragraph on ***humans*** below). However, probably the most common exposure for herbivorous animals grazing within a zone of pollution will be the ingestion of feed contaminated by air pollutants. In this case, inhalation is of secondary importance.

Air pollutants that present a hazard to livestock, therefore, are those that are taken up by vegetation or deposited on the plants. Only a few pollutants have been observed to cause harm to animals. These include arsenic, fluorides, lead, mercury, and molybdenum.

Humans There seems to be little question that, during many of the more serious episodes, air pollution can have a significant effect on health, especially upon the young, elderly, or people already in ill health. Hundreds of excess deaths have been attributed to incidents in London in 1952, 1956, 1957, and 1962; in Donora, Pennsylvania, in 1948; in New York City in 1953, 1963, and 1966; and Bhopal, India in 1989. Many of the people affected were in failing health, and they were generally suffering from lung conditions. In addition, hundreds of thousands of persons have suffered from serious discomfort and inconvenience, including eye irritation and chest pains, during these and other such incidents. Such acute problems are actually the lesser of the health problems. There is considerable evidence of a chronic threat to human health from air pollution. This evidence ranges from the rapid rise of emphysema as a major health problem, through identification of carcinogenic compounds in smog, to statistical evidence that people exposed to polluted atmospheres over extended periods of time suffer from a number of ailments and a reduction in their life span. There may even be a significant indirect exposure to air pollution. As noted above, air pollutants may be deposited onto vegetation or into bodies of water, where they enter the food chain. The impact of such indirect exposures is still under review.

Sufficient evidence is available to indicate that atmospheric pollution in varying degrees does affect health adversely. [Amdur, Melvin, and Drinker, "Effect of Inhalation of Sulfur Dioxide by Man," *Lancet,* **2,** 758 (1953); Barton, Corn, Gee, Vassallo, and Thomas, "Response of Healthy Men to Inhaled Low Concentrations of Gas-Aerosol Mixtures," *Arch. Environ. Health,* **18,** 681 (1969); Bates, Bell, Burnham, Hazucha, and Mantha, "Problems in Studies of Human Exposure to Air Pollutants," *Can. Med. Assoc. J.,* **103,** 833 (1970); Ciocco and

Thompson, "A Follow-Up of Donora Ten Years After: Methodology and Findings," *Am. J. Public Health,* **51,** 155 (1961); Daly, "Air Pollution and Causes of Death," *Br. J. Soc. Med.,* **13,** 14 (1959); Jaffe, "The Biological Effect of Photochemical Air Pollutants on Man and Animals," *Am. J. Public Health,* New York, **57,** 1269 (1967); New York Academy of Medicine, Committee on Public Health, "Air Pollution and Health," *Bull. N.Y. Acad. Med.,* **42,** 588 (1966); Pemberton and Goldberg, "Air Pollution and Bronchitis," *Br. Med. J.,* London, **2,** 567 (1954); Snell and Luchsinger, "Effect of Sulfur Dioxide on Expiratory Flowrates and Total Respiratory Resistance in Normal Human Subjects," *Arch. Environ. Health,* Chicago, **18,** 693 (1969); Speizer and Frank, "A Comparison of Changes in Pulmonary Flow Resistance in Healthy Volunteers Acutely Exposed to SO_2 by Mouth and by Nose," *J. Ind. Med.,* **23** 75 (1966); Stocks, "Cancer and Bronchitis Mortality in Relation to Atmospheric Deposit and Smoke," *Br. Med. J. London,* **1,** 74 (1959); Toyama, "Air Pollution and Its Health Effects in Japan," *Arch. Environ. Health,* Chicago, **8,** 153 (1963); U.K. Ministry of Health, "Mortality and Morbidity During London Fog of December 1952," Report on Public Health and Medical Subjects No. 95, London, 1954; U.S. Public Health Service, "Air Pollution in Donora, Pa.: Preliminary Report," Public Health Bull. 306.] It contributes to excesses of death, increased morbidity, and earlier onset of chronic respiratory diseases. There is evidence of a relationship between the intensity of the pollution and the severity of attributable health effects and a consistency of the relationship between these environmental stresses and diseases of the target organs. Air pollutants can both initiate and aggravate a variety of respiratory diseases including asthma. In fact, the clinical presentation of asthma may be considered an air pollution host-defense disorder brought on by specific airborne irritants: pollens, infectious agents, and gaseous and particulate chemicals. The bronchopulmonary response to these foreign irritants is bronchospasm and hypersecretion; the airways are intermittently and reversibly obstructed.

Air-pollutant effects on neural and sensory functions in humans vary widely. Odorous pollutants cause only minor annoyance; yet, if persistent, they can lead to irritation, emotional upset, anorexia, and mental depression. Carbon monoxide can cause death secondary to the depression of the respiratory centers of the central nervous system. Short of death, repeated and prolonged exposure to carbon monoxide can alter sensory protection, temporal perception, and higher mental functions. Lipid-soluble aerosols can enter the body and be absorbed in the lipids of the central nervous system. Once there, their effects may persist long after the initial contact has been removed. Examples of agents of long-term chronic effects are organic phosphate pesticides and aerosols carrying the metals lead, mercury, and cadmium.

The acute toxicological effects of most air contaminants are reasonably well understood, but the effects of exposure to heterogenous mixtures of gases and particulates at very low concentrations are only beginning to be comprehended. Two general approaches can be used to study the effects of air contaminants on humans: epidemiology, which attempts to associate the effect in large populations with the cause, and laboratory research, which begins with the cause and attempts to determine the effects. Ideally, the two methods should complement each other.

Epidemiology, the more costly of the two, requires great care in planning and often suffers from incomplete data and lack of controls. One great advantage, however, is that moral barriers do not limit its application to humans as they do with some kinds of laboratory research. The method is therefore highly useful and has produced considerable information. Laboratory research is less costly than epidemiology, and its results can be checked against controls and verified by experimental repetition.

A SOURCE-CONTROL-PROBLEM STRATEGY

Strategy Control technology is self-defeating if it creates undesirable side effects in meeting objectives. Air pollution control must be considered in terms of regulatory requirements, total technological systems (equipment and processes), and ecological consequences, such as the problems of treatment and disposal of collected pollutants. It should be noted that the 1990 Clean Air Act Amendments (CAAA) have impacted on the control approach in a significant manner. In particular, the CAAA have placed an increased emphasis on control technology by requiring Best Available Control Technology (BACT) on new major sources and modifications, and by requiring Maximum Achievable Control Technology (MACT) on new and *existing* major sources of Hazardous Air Pollutants (HAPs).

The control strategy for environmental-impact assessment often focuses on five alternatives whose purpose would be the reduction and/or elimination of pollutant emissions:

1. Elimination of the operation entirely or in part
2. Modification of the operation
3. Relocation of the operation
4. Application of appropriate control technology
5. Combinations thereof

In light of the relatively high costs often associated with pollution-control systems, engineers are directing considerable effort toward process modification to eliminate as much of the pollution problem as possible at the source. This includes evaluating alternative manufacturing and production techniques, substituting raw materials, and improving process-control methods. Unfortunately, if there is no alternative, the application of the correct pollution-control equipment is essential. The equipment must be designed to comply with regulatory emission limitations on a continual basis, interruptions being subject to severe penalty depending upon the circumstances. The requirement for design performance on a continual basis places very heavy emphasis on operation and maintenance practices. The escalating costs of energy, labor, and materials can make operation and maintenance considerations even more important than the original capital cost.

Factors in Control-Equipment Selection In order to solve an air-pollution problem, the problem must be defined in detail. A number of factors must be considered prior to selecting a particular piece of air-pollution-control equipment. In general, these factors can be grouped into three categories: environmental, engineering, and economic.

Environmental Factors These include (1) equipment location, (2) available space, (3) ambient conditions, (4) availability of adequate utilities (i.e., power, water, etc.) and ancillary-system facilities (i.e., waste treatment and disposal, etc.), (5) maximum allowable emission (air pollution codes), (6) aesthetic considerations (i.e., visible steam or water-vapor plume, etc.), (7) contributions of the air-pollution-control system to wastewater and land pollution, and (8) contribution of the air-pollution-control system to plant noise levels.

Engineering Factors These include:

1. Contaminant characteristics (e.g., physical and chemical properties, concentration, particulate shape and size distribution [in the case of particulates], chemical reactivity, corrosivity, abrasiveness, and toxicity)

2. Gas-stream characteristics (e.g., volume flow rate, temperature, pressure, humidity, composition, viscosity, density, reactivity, combustibility, corrosivity, and toxicity)

3. Design and performance characteristics of the particular control system (i.e., size and weight, fractional efficiency curves [in the case of particulates]), mass-transfer and/or contaminant-destruction capability (in the case of gases or vapors), pressure drop, reliability, turndown capability, power requirements, utility requirements, temperature limitations, maintenance requirements, operating cycles (including startup and shutdown) and flexibility toward complying with more stringent air-pollution codes.

Economic Factors These include capital cost (equipment, installation, engineering, etc.), operating cost (utilities, maintenance, etc.), emissions fees, and life-cycle cost over the expected equipment lifetime.

Comparing Control-Equipment Alternatives The final choice in equipment selection is usually dictated by the equipment capable of achieving compliance with regulatory codes at the lowest uniform annual cost (amortized capital investment plus operation and maintenance costs). To compare specific control-equipment alternatives, knowledge of the particular application and site is essential. A preliminary screening, however, may be performed by reviewing the advantages and disadvantages of each type of air-pollution-control

equipment. General advantages and disadvantages of the most popular types of air-pollution equipment for gases and particulates are presented in Tables 25-13 through 25-25. Other activities that must be accomplished before final compliance is achieved are presented in Table 25-26.

In addition to using annualized cost comparisons in evaluating an air-pollution-control (APC) equipment installation, the impact of the 1990 Clean Air Act Amendments (CAAA) and resulting regulations also must be included in the evaluation. The CAAA prescribes specific pollution-control requirements for particular industries and locations. As an example, the CAAA requires that any major stationary source or

TABLE 25-13 Advantages and Disadvantages of Cyclone Collectors

Advantages

1. Low cost of construction
2. Relatively simple equipment with few maintenance problems
3. Relatively low operating pressure drops (for degree of particulate removal obtained) in the range of approximately 2- to 6-in water column
4. Temperature and pressure limitations imposed only by the materials of construction used
5. Collected material recovered dry for subsequent processing or disposal
6. Relatively small space requirements

Disadvantages

1. Relatively low overall particulate collection efficiencies, especially on particulates below 10 μm in size
2. Inability to handle tacky materials

TABLE 25-14 Advantages and Disadvantages of Wet Scrubbers

Advantages

1. No secondary dust sources
2. Relatively small space requirements
3. Ability to collect gases as well as particulates (especially "sticky" ones)
4. Ability to handle high-temperature, high-humidity gas streams
5. Capital cost low (if wastewater treatment system not required)
6. For some processes, gas stream already at high pressures (so pressure-drop considerations may not be significant)
7. Ability to achieve high collection efficiencies on fine particulates (however, at the expense of pressure drop)
8. Ability to handle gas streams containing flammable or explosive materials

Disadvantages

1. Possible creation of water-disposal problem
2. Product collected wet
3. Corrosion problems more severe than with dry systems
4. Steam plume opacity and/or droplet entrainment possibly objectionable
5. Pressure-drop and horsepower requirements possibly high
6. Solids buildup at the wet-dry interface possibly a problem
7. Relatively high maintenance costs
8. Must be protected from freezing
9. Low exit gas temperature reduces exhaust plume dispersion
10. Moist exhaust gas precludes use of most additional controls

TABLE 25-15 Advantages and Disadvantages of Dry Scrubbers

Advantages

1. No wet sludge to dispose of
2. Relatively small space requirements
3. Ability to collect acid gases at high efficiencies
4. Ability to handle high-temperature gas streams
5. Dry exhaust allows addition of fabric filter to control particulate

Disadvantages

1. Acid gas control efficiency not as high as with wet scrubber
2. No particulate collection—dry scrubber generates particulate
3. Corrosion problems more severe than with dry systems
4. Solids buildup at the wet-dry interface possibly a problem
5. Relatively high maintenance costs
6. Must be protected from freezing
7. Low exit gas temperature reduces exhaust plume dispersion

TABLE 25-16 Advantages and Disadvantages of Electrostatic Precipitators

Advantages

1. Extremely high particulate (coarse and fine) collection efficiencies attainable (at a relatively low expenditure of energy)
2. Collected material recovered dry for subsequent processing or disposal
3. Low pressure drop
4. Designed for continuous operation with minimum maintenance requirements
5. Relatively low operating costs
6. Capable of operation under high pressure (to 150 lbf/in^2) or vacuum conditions
7. Capable of operation at high temperatures [to 704°C(1300°F)]
8. Relatively large gas flow rates capable of effective handling

Disadvantages

1. High capital cost
2. Very sensitive to fluctuations in gas-stream conditions (in particular, flows, temperature, particulate and gas composition, and particulate loadings)
3. Certain particulates difficult to collect owing to extremely high- or low-resistivity characteristics
4. Relatively large space requirements required for installation
5. Explosion hazard when treating combustible gases and/or collecting combustible particulates
6. Special precautions required to safeguard personnel from the high voltage
7. Ozone produced by the negatively charged discharge electrode during gas ionization
8. Relatively sophisticated maintenance personnel required
9. Gas ionization may cause dissociation of gas stream constituents and result in creation of toxic byproducts
10. Sticky particulates may be difficult to remove from plates
11. Not effective in capturing some contaminants that exist as vapors at high temperatures (e.g., heavy metals, dioxins)

TABLE 25-17 Advantages and Disadvantages of Fabric-Filter Systems

Advantages

1. Extremely high collection efficiency on both coarse and fine (submicrometer) particles
2. Relatively insensitive to gas-stream fluctuation; efficiency and pressure drop relatively unaffected by large changes in inlet dust loadings for continuously cleaned filters
3. Filter outlet air capable of being recirculated within the plant in many cases (for energy conservation)
4. Collected material recovered dry for subsequent processing or disposal
5. No problems with liquid-waste disposal, water pollution, or liquid freezing
6. Corrosion and rusting of components usually not problems
7. No hazard of high voltage, simplifying maintenance and repair and permitting collection of flammable dusts
8. Use of selected fibrous or granular filter aids (precoating), permitting the high-efficiency collection of submicrometer smokes and gaseous contaminants
9. Filter collectors available in a large number of configurations, resulting in a range of dimensions and inlet and outlet flange locations to suit installment requirements
10. Relatively simple operation

Disadvantages

1. Temperatures much in excess of 288°C (550°F) requiring special refractory mineral or metallic fabrics that are still in the developmental stage and can be very expensive
2. Certain dusts possibly requiring fabric treatments to reduce dust seeping or, in other cases, assist in the removal of the collected dust
3. Concentrations of some dusts in the collector (~50 g/m^3) forming a possible fire or explosion hazard if a spark or flame is admitted by accident; possibility of fabrics burning if readily oxidizable dust is being collected
4. Relatively high maintenance requirements (bag replacement, etc.)
5. Fabric life possibly shortened at elevated temperatures and in the presence of acid or alkaline particulate or gas constituents
6. Hygroscopic materials, condensation of moisture, or tarry adhesive components possibly causing crusty caking or plugging of the fabric or requiring special additives
7. Replacement of fabric, possibly requiring respiratory protection for maintenance personnel
8. Medium pressure-drop requirements, typically in the range 4- to 10-in water column

TABLE 25-18 Advantages and Disadvantages of Absorption Systems (Packed and Plate Columns)

Advantages
1. Relatively low pressure drop
2. Standardization in fiberglass-reinforced plastic (FRP) construction permitting operation in highly corrosive atmospheres
3. Capable of achieving relatively high mass-transfer efficiencies
4. Increasing the height and/or type of packing or number of plates capable of improving mass transfer without purchasing a new piece of equipment
5. Relatively low capital cost
6. Relatively small space requirements
7. Ability to collect particulates as well as gases
8. Collected substances may be recovered by distillation

Disadvantages
1. Possibility of creating water (or liquid) disposal problem
2. Product collected wet
3. Particulates deposition possibly causing plugging of the bed or plates
4. When FRP construction is used, sensitive to temperature
5. Relatively high maintenance costs
6. Must be protected from freezing

TABLE 25-19 Comparison of Plate and Packed Columns

Packed column
1. Lower pressure drop
2. Simpler and cheaper to construct
3. Preferable for liquids with high-foaming tendencies

Plate column
1. Less susceptible to plugging
2. Less weight
3. Less of a problem with channeling
4. Temperature surge resulting in less damage

TABLE 25-20 Advantages and Disadvantages of Adsorption Systems

Advantages
1. Possibility of product recovery
2. Excellent control and response to process changes
3. No chemical-disposal problem when pollutant (product) recovered and returned to process
4. Capability of systems for fully automatic, unattended operation
5. Capability to remove gaseous or vapor contaminants from process streams to extremely low levels

Disadvantages
1. Product recovery possibly requiring an exotic, expensive distillation (or extraction) scheme
2. Adsorbent progressively deteriorating in capacity as the number of cycles increases
3. Adsorbent regeneration requiring a steam or vacuum source
4. Relatively high capital cost
5. Prefiltering of gas stream possibly required to remove any particulate capable of plugging the adsorbent bed
6. Cooling of gas stream possibly required to get to the usual range of operation (less than 49°C [120°F])
7. Relatively high steam requirements to desorb high-molecular-weight hydrocarbons
8. Spent adsorbent may be considered a hazardous waste
9. Some contaminants may undergo a violent exothermic reaction with the adsorbent

major modification plan that is subject to Prevention of Significant Deterioration (PSD) requirements must under go a Best Available Control Technology (BACT) analysis. The BACT analysis is done on a case-by-case basis. The process involves evaluating the possible types of air-pollution-control equipment that could be used for technology and energy and in terms of the environment and economy. The analysis uses a top-down approach that lists all available control technologies in descending order of effectiveness. The most stringent technology is chosen unless it can be demonstrated that, due to tech-

TABLE 25-21 Advantages and Disadvantages of Combustion Systems

Advantages
1. Simplicity of operation
2. Capability of steam generation or heat recovery in other forms
3. Capability for virtually complete destruction of organic contaminants

Disadvantages
1. Relatively high operating costs (particularly associated with fuel requirements)
2. Potential for flashback and subsequent explosion hazard
3. Catalyst poisoning (in the case of catalytic incineration)
4. Incomplete combustion, possibly creating potentially worse pollution problems
5. Even complete combustion may produce SO_2, NO_x, and CO_2
6. High temperature components and exhaust may be hazardous to maintenance personnel and birds
7. High maintenance requirements—especially if operation is cyclic

TABLE 25-22 Advantages and Disadvantages of Condensers

Advantages
1. Pure product recovery (in the case of indirect-contact condensers)
2. Water used as the coolant in an indirect-contact condenser (i.e., shell-and-tube heat exchanger), not in contact with contaminated gas stream, and is reusable after cooling
3. May be used to produce vacuum to remove contaminants from process

Disadvantages
1. Relatively low removal efficiency for gaseous contaminants (at concentrations typical of pollution-control applications)
2. Coolant requirements possibly extremely expensive
3. Direct-contact condenser may produce water discharge problems

TABLE 25-23 Advantages and Disadvantages of Biofiltration

Advantages
1. Uses natural biological processes and materials
2. Relatively simple and economical
3. High destruction efficiencies for oxygen-rich, low-contaminant concentration gas streams
4. Waste products are CO_2 and water

Disadvantages
1. Raw gas must not be lethal to microorganisms
2. Gas stream must be maintained at proper temperature and humidity
3. Heavy particulate loadings can damage pore structure of filter bed

TABLE 25-24 Advantages and Disadvantages of Membrane Filtration

Advantages
1. Low energy utilization
2. Modular design
3. Low capital costs
4. Low maintenance
5. Superior separation ability

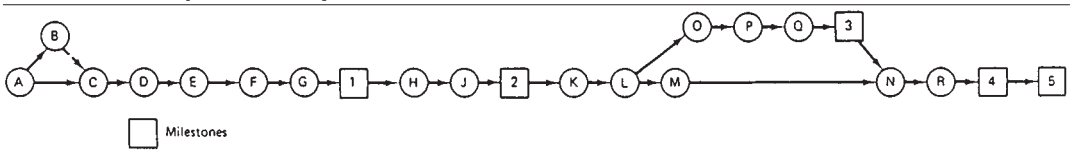
Disadvantages
1. Potential particulate fouling problems if not properly designed

TABLE 25-25 Advantages and Disadvantages of Selective Catalytic Reduction of Nitrogen Oxides

Advantages
1. Capable of 90% NO_x removal
2. Uses readily available urea reagent
3. Exhaust products are N_2 and water

Disadvantages
1. Spent catalyst may be considered hazardous waste
2. Gas stream must be maintained at proper temperature and humidity
3. Heavy particulate loadings can damage pore structure of filter bed

TABLE 25-26 Compliance Activity and Schedule Chart



Milestones

1. Date of submittal of final control plan to appropriate agency
2. Date of award of control-device contract
3. Date of initiation of on-site construction or installation of emission-control equipment
4. Date by which on-site construction or installation of emission-control equipment is completed
5. Date by which final compliance is achieved

Activities

Designation	Activity	Designation	Activity
A-C	Preliminary investigation.	K-L	Review and approval of assembly drawings.
A-B	Source tests, if necessary.	L-M	Vendor prepares fabrication drawings.
C-D	Evaluate control alternatives.	M-N	Fabricate control device.
D-E	Commit funds for total program.	L-O	Prepare engineering drawings.
E-F	Prepare preliminary control plan and compliance schedule for agency.	O-P	Procure construction bids.
		P-Q	Evaluate construction bids.
F-G	Agency review and approval.	Q-3	Award construction contract.
G-I	Finalize plans and specifications.	3-N	On-site construction.
I-H	Procure control-device bids.	N-R	Install control device.
H-J	Evaluate control-device bids.	R-4	Complete construction (system tie-in).
J-2	Award control-device contract.	4-5	Startup, shakedown, source test.
2-K	Vendor prepares assembly drawings.		

nical, energy, environmental, or economic considerations, this type of APC technology is not feasible.

The 1990 CAAA introduced a new level of control for hazardous (toxic) air pollutants (HAPs). As a result, EPA has identified 189 HAPs for regulation. Rather than rely upon ambient air quality standards to set acceptable exposures to HAPs, the CAAA requires that EPA promulgate through the end of the decade Maximum Achievable Control Technology (MACT) standards for controlling HAPs emitted from specified industries. These standards are based on the level of control established by the best performing 12 percent of industries in each of the categories identified by EPA.

DISPERSION FROM STACKS

Stacks discharging to the atmosphere have long been the most common industrial method of disposing of waste gases. The concentrations to which humans, plants, animals, and structures are exposed at ground level can be reduced significantly by emitting the waste gases from a process at great heights. Although tall stacks may be effective in lowering the ground-level concentration of pollutants, they do not in themselves reduce the amount of pollutants released into the atmosphere. However, in certain situations, their use can be the most practical and economical way of dealing with an air-pollution problem.

Preliminary Design Considerations To determine the acceptability of a stack as a means of disposing of waste gases, the acceptable ground-level concentration (GLC) of the pollutant or pollutants must be determined. The topography of the area must also be considered so that the stack can be properly located with respect to buildings and hills that might introduce a factor of air turbulence into the operation of the stack. Awareness of the meteorological conditions prevalent in the area, such as the prevailing winds, humidity, and rainfall, is also essential. Finally, an accurate knowledge of the constituents of the waste gas and their physical and chemical properties is paramount.

Wind Direction and Speed Wind direction is measured at the height at which the pollutant is released, and the mean direction will indicate the direction of travel of the pollutants. In meteorology, it is conventional to consider the wind direction as the direction from which the wind blows; therefore, a northwest wind will move pollutants to the southeast of the source.

The effect of wind speed is twofold: (1) Wind speed will determine the travel time from a source to a given receptor; and (2) wind speed will affect dilution in the downwind direction. Generally, the concentration of air pollutants downwind from a source is inversely proportional to wind speed.

Wind speed has velocity components in all directions so that there are vertical motions as well as horizontal ones. These random motions of widely different scales and periods are essentially responsible for the movement and diffusion of pollutants about the mean downwind path. These motions can be considered atmospheric turbulence. If the scale of a turbulent motion (i.e., the size of an eddy) is larger than the size of the pollutant plume in its vicinity, the eddy will move that portion of the plume. If an eddy is smaller than the plume, its effect will be to diffuse or spread out the plume. This diffusion caused by eddy motion is widely variable in the atmosphere, but even when the effect of this diffusion is least, it is in the vicinity of three orders of magnitude greater than diffusion by molecular action alone.

Mechanical turbulence is the induced-eddy structure of the atmosphere due to the roughness of the surface over which the air is passing. Therefore, the existence of trees, shrubs, buildings, and terrain features will cause mechanical turbulence. The height and spacing of the elements causing the roughness will affect the turbulence. In general, the higher the roughness elements, the greater the mechanical turbulence. In addition, mechanical turbulence increases as wind speed increases.

Thermal turbulence is turbulence induced by the stability of the atmosphere. When the Earth's surface is heated by the sun's radiation, the lower layer of the atmosphere tends to rise and thermal turbulence becomes greater, especially under conditions of light wind. On clear nights with wind, heat is radiated from the Earth's surface, resulting in the cooling of the ground and the air adjacent to it. This results in extreme stability of the atmosphere near the Earth's surface. Under these conditions, turbulence is at a minimum. Attempts to relate different measures of turbulence of the wind (or stability of the atmosphere) to atmospheric diffusion have been made for some time. The measurement of atmospheric stability by temperature-difference measurements on a tower is frequently utilized as an indirect measure of turbulence, particularly when climatological estimates of turbulence are desired.

Lapse Rate and Atmospheric Stability Apart from mechanical interference with the steady flow of air caused by buildings and other obstacles, the most important factor that influences the degree of turbulence and hence the speed of diffusion in the lower air is the varia-

tion of temperature with height above the ground, referred to as the "lapse rate." The dry-adiabatic lapse rate (DALR) is the temperature change for a rising parcel of dry air. The dry-adiabatic lapse rate can be approximated as −1° C per 100 m, or $dT/dz = -10^{-2}$ °C/m or −5.4° F/1000 ft. If the rising air contains water vapor, the cooling due to adiabatic expansion will result in the relative humidity being increased, and saturation may be reached. Further ascent would then lead to condensation of water vapor, and the latent heat thus released would reduce the rate of cooling of the rising air. The buoyancy force on a warm-air parcel is caused by the difference between its density and that of the surrounding air. The perfect-gas law shows that, at a fixed pressure (altitude), the temperature and density of an air parcel are inversely related; temperature is normally used to determine buoyancy because it is easier to measure than density. If the temperature gradient (lapse rate) of the atmosphere is the same as the adiabatic lapse rate, a parcel of air displaced from its original position will expand or contract in such a manner that its density and temperature remain the same as its surroundings. In this case there will be no buoyancy forces on the displaced parcel, and the atmosphere is termed "neutrally stable."

If the atmospheric temperature decreases faster with increasing altitude than the adiabatic lapse rate (superadiabatic), a parcel of air displaced upward will have a higher temperature than the surrounding air. Its density will be lower, giving it a net upward buoyancy force. The opposite situation exists if the parcel of air is displaced downward, and the parcel experiences a downward buoyancy force. Once a parcel of air has started moving up or down, it will continue to do so, causing unstable atmospheric conditions. If the temperature decreases more slowly with increasing altitude than the adiabatic lapse rate, a displaced parcel of air experiences a net restoring force. The buoyancy forces then cause stable atmospheric conditions (see Fig. 25-4).

Strongly stable lapse rates are commonly referred to as *inversions.* The strong stability inhibits mixing across the inversion layer. Normally these conditions of strong stability extend for only several hundred meters vertically. The vertical extent of the inversion is referred to as the *inversion depth.* Two distinct types are observed: the ground-level inversion, caused by radiative cooling of the ground at night, and inversions aloft, occurring between 500 and several thousand meters above the ground (see Fig. 25-5). Some of the more common lapse-rate profiles with the corresponding effect on stackplumes are presented in Fig. 25-6.

From the viewpoint of air pollution, both stable surface layers and low-level inversions are undesirable because they minimize the rate of dilution of contaminants in the atmosphere. Even though the surface layer may be unstable, a low-level inversion will act as a barrier to vertical mixing, and contaminants will accumulate in the surface layer below the inversion. Stable atmospheric conditions tend to be more frequent and longest in persistence in the autumn, but inversions and stable lapse rates are prevalent at all seasons of the year.

Design Calculations For a given stack height, the calculational sequence begins by first estimating the effective height of the emission, employing an applicable plume-rise equation. The maximum GLC may then be determined by using an appropriate atmospheric-diffusion equation. A simple comparison of the calculated GLC for the particular pollutant with the maximum GLC permitted by the local air-pollution codes dictates whether the stack is operating satisfactorily.

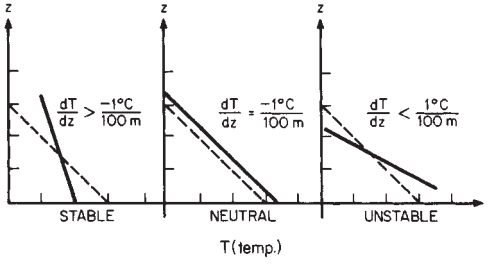


FIG. 25-4 Stability criteria with measured lapse rate.

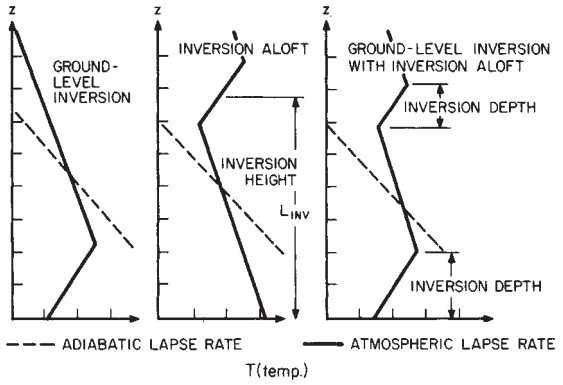


FIG. 25-5 Characteristic lapse rates under inversion conditions.

Conversely, with knowledge of the maximum acceptable GLC standards, a stack that will satisfy these standards can be properly designed.

Effective Height of an Emission The effective height of an emission rarely corresponds to the physical height of the stack. If the plume is caught in the turbulent wake of the stack or of buildings in the vicinity of the stack, the effluent will be mixed rapidly downward toward the ground. If the plume is emitted free of these turbulent zones, a number of source emission characteristics and meteorological factors influence the rise of the plume. The source emission characteristics include the gas flow rate and the temperature of the effluent at the top of the stack and the diameter of the stack opening. The meteorological factors influencing plume rise include wind speed, air temperature, shear of the wind speed with height, and atmospheric stability. No theory on plume rise presently takes into account all of these variables. Most of the equations that have been formulated for computing the effective height of an emission are semi-empirical. When considering any of these plume-rise equations, it is important to evaluate each in terms of the assumptions made and the circumstances existing at the time that the particular correlation was formulated. The formulas generally are not applicable to tall stacks (above 305 m [1000 ft] effective height).

The effective stack height (equivalent to the effective height of the emission) is the sum of the actual stack height, the plume rise due to the exhaust velocity (momentum) of the issuing gases, and the buoyancy rise, which is a function of the temperature of the gases being emitted and the atmospheric conditions.

Some of the more common plume-rise equations have been summarized by Buonicore and Theodore (*Industrial Control Equipment for Gaseous Pollutants,* vol. 2, CRC Press, Boca Raton, Florida, 1975) and include:

- ASME, *Recommended Guide for the Prediction of the Dispersion of Airborne Effluents,* ASME, New York, 1968.
- Bosanquet-Carey-Halton, *Proc. Inst. Mech. Eng.* (*London*), **162,** 355 (1950).
- Briggs, *Plume Rise,* AEC Critical Review ser., U.S. Atomic Energy Commission, Div. Tech. Inf.
- Brummage et al., *The Calculation of Atmospheric Dispersion from a Stack,* CONCAWE, The Hague, 1966.
- Carson and Moses, *J. Air Pollut. Control Assoc.,* **18,** 454 (1968) and **19,** 862 (1969).
- Csnaday, *Int. J. Air Water Pollut.,* **4,** 47 (1961).
- Davison-Bryant, *Trans. Conf. Ind. Wastes,* 14th Ann. Meet. Ind. Hyg. Found. Am., **39,** 1949.
- Holland, *Workbook of Atmospheric Dispersion Estimates,* U.S. EPA Publ. AP-26, 1970.
- Lucas, Moore, and Spurr, *Int. J. Air Water Pollut.,* **7,** 473 (1963).
- Montgomery et al., *J. Air Pollut. Control Assoc.,* **22**(10), 779, TVA (1972).
- Stone and Clarke, *British Experience with Tall Stacks for Air Pollution Control on Large Fossil-Fueled Power Plants,* American Power Conference, Chicago, 1967.

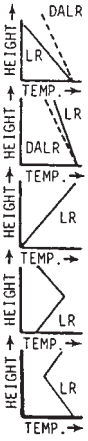
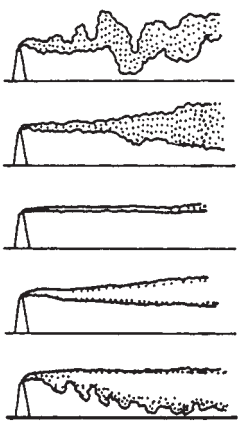
Temperature gradient	Observation	Description
		Strong lapse—looping (unstable) This is usually a fair-weather daytime condition, since strong solar heating of the ground is required. Looping is not favored by cloudiness, snow cover, or strong winds. Weak lapse—coning (slightly unstable or neutral) This is usually favored by cloudy and windy conditions and may occur day or night. In dry climates it may occur infrequently, and in cloudy climates it may be the most frequent type observed. Inversion—fanning (stable) This is principally a nighttime condition. It is favored by light winds, clear skies, and snow cover. The condition may persist in some climates for several days at a time during winter, especially in the higher latitudes. Inversion below, lapse aloft—lofting (transition from unstable to stable) This condition occurs during transition from lapse to inversion and should be observed most frequently near sunset; it may be very transitory or persist for several hours. The shaded zone of strong effluent concentration is caused by trapping by the inversion of effluent carried into the stable layer by turbulent eddies that penetrate the layer for a short distance. Lapse below, inversion aloft—fumigation (transition from stable to unstable) This occurs when the nocturnal inversion is dissipated by heat from the morning sun. The lapse layer usually starts at the ground and works its way upward (less rapidly in winter than in summer). Fumigation may also occur in sea-breeze circulations during late morning or early afternoon. The shaded zone of strong concentration is that portion of the plume which has not yet been mixed downward.

FIG. 25-6 Lapse-rate characteristics of atmospheric-diffusion transport of stack emissions.

• Stumke, *Staub,* **23,** 549 (1963).

See also:

• Briggs, G. A., *Plume Rise Predications: Lectures on Air Pollution and Environmental Impact Analyses,* Workshop Proceedings, American Meteorological Society, Boston, Massachusetts, 1975, pp. 59–111.

• Randerson, Darryl (ed.), *Plume Rise and Bouyancy Effects, Atmospheric Science and Power Production,* DOE Report DOE/TIC-27601, 1981.

Maximum Ground-Level Concentrations The effective height of an emission having been determined, the next step is to study its path downward by using the appropriate atmospheric-dispersion formula. Some of the more popular atmospheric-dispersion calculational procedures have been summarized by Buonicore and Theodore (op. cit.) and include:

• Bosanquet-Pearson model [Pasquill, *Meteorol. Mag.,* **90,** 33, 1063 (1961), and Gifford, *Nucl. Saf.,* **2,** 4, 47 (1961).]

• Sutton model [*Q.J.R. Meteorol. Soc.,* **73,** 257 (1947).]

• TVA Model [Carpenter et al., *J. Air Pollut. Control Assoc.,* **21**(8), (1971), and Montgomery et al., *J. Air Pollut. Control Assoc.,* **23**(5), 388 (1973).]

See also:

• Bornstein et al., *Simulation of Urban Barrier Effects on Polluted Urban Boundary Layers Using the Three-Dimensional URBMET\TVM Model with Urban Topography,* Air Pollution Proceedings, 1993.

• EPA, *Guidance on the Application of Refined Dispersion Models for Air Toxins Releases,* EPA-450/4-91-007.

• Zannetti, Paolo, *Air Pollution Modeling: Theories, Computational Methods, and Available Software,* Van Nostrand, Reinhold, New York, 1990.

• Zannetti, Paolo, *Numerical Simulation Modeling of Air Pollution: An Overview,* Ecological Physical Chemistry, 2d International Workshop, May 1992.

Miscellaneous Effects

Evaporative Cooling When effluent gases are washed to absorb certain constituents prior to emission, the gases are cooled and become saturated with water vapor. Upon release of the gases, further cooling due to contact with cold surfaces of ductwork or stack is likely. This cooling causes water droplets to condense in the gas stream. Upon release of the gases from the stack, the water droplets evaporate, withdrawing the latent heat of vaporization from the air and cooling the plume. The resulting negative buoyancy reduces the effective stack height. The result may be a plume (with a greater density than that of the ambient atmosphere) that will fall to the ground. If any pollutant remains after scrubbing, its full effect will be felt on the ground in the vicinity of the stack.

Aerodynamic Downwash Should the stack exit velocity be too low as compared with the speed of the crosswind, some of the effluent can be pulled downward by the low pressure on the lee side of the stack. This phenomenon, known as "stack-tip downwash," can be minimized by keeping the exit velocity greater than the mean wind speed (i.e., typically twice the mean wind speed). Another way to minimize stack-tip downwash is to fit the top of the stack with a flat disc that extends for at least one stack diameter outward from the stack.

If it becomes necessary to increase the stack-gas exit velocity to avoid downwash, it may be necessary to remodel the stack exit. A venturi-nozzle design has been found to be the most effective. This design also keeps pressure losses to a minimum.

Building Downwash A review must be conducted for each stack to determine if building downwash effects need to be considered. Atmospheric flow is disrupted by aerodynamic forces in the immediate vicinity of structures or terrain obstacles. The disrupted flow near either building structures or terrain obstacles can both enhance the vertical dispersion of emissions from the source and reduce the effective height of the emissions from the source, resulting in an increase in the maximum GLC.

EPA Air Dispersion Models EPA addresses modeling techniques in the "Guideline on Air Quality Models" (GAQM-Revised. EPA-450/2-78-027R, July 1986). Several computational models are available for performing air quality analyses. However, there is no one model capable of properly addressing all conceivable modeling situations. The EPA recommends a case-by-case approach to selection of appropriate models. All models incorporate assumptions that are designed to predict conservative results. Since the general intention of modeling is to determine if the maximum GLC is below regulatory limits, modeling is performed beginning with the simpler models with the most conservative assumptions and proceeding to more complex models with more sophisticated input data. Input data includes source characteristics, topography, and meteorological factors.

The air quality modeling procedures can be categorized into four generic classes: Gaussian, numerical, statistical, and physical. Gaussian models are the most widely used techniques for estimating the impact from nonreactive pollutants. Numerical models are more appropriate for urban applications involving reactive pollutants. In cases where the scientific understanding of the physical or chemical processes involved is lacking, a statistical modeling approach may be necessary. Statistical modeling involves the collection of a large number of site-specific measurements that are evaluated to develop a predictive modeling tool that is limited to use at that site. Physical modeling is performed using a wind tunnel or other fluid modeling

facility. Physical modeling may be useful for complex flow situations, such as building, terrain, or stack downwash conditions, plume impact on elevated terrain, diffusion in an urban environment, or diffusion in complex terrain. It is generally limited to use within a few square kilometers surrounding the source.

Most modeling can be performed using Gaussian models. The simplest Gaussian model is the EPA SCREEN2 model. This is an interactive computational model that incorporates algorithms for calculating maximum GLC in simple terrain (below stack top) or complex terrain (above stack top) considering downwash and cavity effects. The SCREEN2 model is designed for single source modeling. A set of conservative meteorological conditions is contained within the model.

The Industrial Source Complex (ISC2) model allows for modeling to be performed in simple terrain for multiple sources and allows for use of real meteorological data. Complex I is a screening level model commonly used in complex terrain modeling. This model may use real meteorological data and allows for modeling multiple sources. The Complex Terrain Dispersion Model Plus Algorithms for Unstable Situations (CTDMPLUS) is a refined point source Gaussian air quality model for use in all stability conditions for complex terrain applications. Its use of meteorological and terrain data is different from other EPA models. CTDMPLUS requires the parameterization of individual hill shapes using a terrain preprocessor. CTSCREEN is a screening version of CTDMPLUS. It contains the same algorithms but is run with synthetic meteorological data.

SOURCE CONTROL OF GASEOUS EMISSIONS

There are four chemical-engineering unit operations commonly used for the control of gaseous emissions:

1. *Absorption.* Sec. 4, "Thermodynamics"; and Sec. 18, "Liquid Gas Systems." For plate columns, see Sec. 18, "Gas-Liquid Contacting: Plate Columns." For packed columns, see Sec. 18, "Gas-Liquid Contacting: Packed Columns."
2. *Adsorption.* See Sec. 16, "Adsorption and Ion Exchange."
3. *Combustion.* See Sec. 9, "Heat Generation" and "Fired Process Equipment." For incinerators, see material under these subsections.
4. *Condensation.* See Sec. 10, "Heat Transmission"; Sec. 11, "Heat-Transfer Equipment"; and Sec. 12, "Evaporative Cooling." For direct-contact condensers, See Sec. 11, "Evaporator Accessories"; and Sec. 12, "Evaporative Cooling." For indirect-contact condensers, see Sec. 10, "Heat Transfer with Change of Phase" and "Thermal Design of Heat-Transfer Equipment"; and Sec. 11, "Shell and Tube Heat Exchangers" and "Other Heat Exchangers for Liquids and Gases."

These operations, which are routine chemical engineering operations, have been treated extensively in other sections of this handbook.

There are three additional chemical engineering unit operations that are increasing in use in recent years. They are:

1. *Biofiltration*
2. *Membrane filtration*
3. *Selective catalytic reduction*

and are discussed further in this section.

Absorption The engineering design of gas absorption equipment must be based on a sound application of the principles of diffusion, equilibrium, and mass transfer as developed in Secs. 5 and 14 of the handbook. The main requirement in equipment design is to bring the gas into intimate contact with the liquid; that is, to provide a large interfacial area and a high intensity of interface renewal and to minimize resistance and maximize driving force. This contacting of the phases can be achieved in many different types of equipment, the most important being packed and plate columns. The final choice between them rests with the various criteria that must be met. For example, if the pressure drop through the column is large enough that compression costs become significant, a packed column may be preferable to a plate-type column because of the lower pressure drop.

In most processes involving the absorption of a gaseous pollutant from an effluent gas stream, the gas stream is the processed fluid; hence, its inlet condition (flow rate, composition, and temperature) are usually known. The temperature and composition of the inlet liquid and the composition of the outlet gas are usually specified. The main objectives in the design of an absorption column, then, are the determination of the solvent flow rate and the calculation of the principal dimensions of the equipment (column diameter and height to accomplish the operation). These objectives can be obtained by evaluating, for a selected solvent at a given flow rate, the number of theoretical separation units (stage or plates) and converting them into practical units column heights or number of actual plates by means of existing correlations.

The general design procedure consists of a number of steps to be taken into consideration. These include:

1. Solvent selection
2. Equilibrium-data evaluation
3. Estimation of operating data (usually consisting of a mass and energy in which the energy balance decides whether the absorption balance can be considered isothermal or adiabatic)
4. Column selection (should the column selection not be obvious or specified, calculations must be carried out for the different types of columns and the final based on economic considerations)
5. Calculation of column diameter (for packed columns, this is usually based on flooding conditions, and, for plate columns, on the optimum gas velocity or the liquid-handling capacity of the plate)
6. Estimation of column height or number of plates (for packed columns, column height is obtained by multiplying the number of transfer units, obtained from a knowledge of equilibrium and operating data, by the height of a transfer unit; for plate columns, the number of theoretical plates determined from the plot of equilibrium and operating lines is divided by the estimated overall plate efficiency to give the number of actual plates, which in turn allows the column height to be estimated from the plate spacing)
7. Determination of pressure drop through the column (for packed columns, correlations dependent of packing type, column-operating data, and physical properties of the constituents involved are available to estimate the pressure drop through the packing; for plate columns, the pressure drop per plate is obtained and multiplied by the number of plates)

Solvent Selection The choice of a particular solvent is most important. Frequently, water is used, as it is very inexpensive and plentiful, but the following properties must also be considered:

1. *Gas solubility.* A high gas solubility is desired, since this increases the absorption rate and minimizes the quantity of solvent necessary. Generally, solvents of a chemical nature similar to that of the solute to be absorbed will provide good solubility.
2. *Volatility.* A low solvent vapor pressure is desired, since the gas leaving the absorption unit is ordinarily saturated with the solvent, and much may thereby be lost.
3. *Corrosiveness.*
4. *Cost.*
5. *Viscosity.* Low viscosity is preferred for reasons of rapid absorption rates, improved flooding characteristics, lower pressure drops, and good heat-transfer characteristics.
6. *Chemical stability.* The solvent should be chemically stable and, if possible, nonflammable.
7. *Toxicity.*
8. *Low freezing point.* If possible, a low freezing point is favored, since any solidification of the solvent in the column makes the column inoperable.

Equipment The principal types of gas-absorption equipment may be classified as follows:

1. Packed columns (continuous operation)
2. Plate columns (staged operations)
3. Miscellaneous

Of the three categories, the packed column is by far the most commonly used for the absorption of gaseous pollutants. Miscellaneous gas-absorption equipment could include acid gas scrubbers that are commonly classified as either "wet" or "dry." In wet scrubber systems, the absorption tower uses a lime-based sorbent liquor that reacts with the acid gases to form a wet/solid by-product. Dry scrubbers can be grouped into three catagories: (1) spray dryers; (2) circulating spray dryers; and (3) dry injection. Each of these systems yields a dry product that can be captured with a fabric filter baghouse downstream and

thus avoids costly wastewater treatment systems. The baghouse is highly efficient in capturing the particulate emissions, and a portion of the overall acid gas removal has been found to occur within the baghouse. Additional information may be found by referring to the appropriate sections in this *handbook* and the many excellent texts available, such as McCabe and Smith, *Unit Operations of Chemical Engineering,* 3d ed., McGraw-Hill, New York, 1976; Sherwood and Pigford, *Absorption and Extraction,* 2d ed., McGraw-Hill, New York, 1952; Smith, *Design of Equilibrium Stage Processes,* McGraw-Hill, New York, 1963; Treybal, *Mass Transfer Operations,* 3d ed., McGraw-Hill, New York, 1980; McKenna, Mycock, and Theodore, *Handbook of Air Pollution Control Engineering and Technology,* CRC Press, Boca Raton, Florida, 1995; Theodore and Allen, *Air Pollution Control Equipment,* ETSI Prof. Training Inst., Roanoke, Virginia, 1993.

Adsorption The design of gas-adsorption equipment is in many ways analogous to the design of gas-absorption equipment, with a solid adsorbent replacing the liquid solvent (see Secs. 16 and 19). Similarity is evident in the material- and energy-balance equations as well as in the methods employed to determine the column height. The final choice, as one would expect, rests with the overall process economics.

Selection of Adsorbent Industrial adsorbents are usually capable of adsorbing both organic and inorganic gases and vapors. However, their preferential adsorption characteristics and other physical properties make each of them more or less specific for a particular application. General experience has shown that, for the adsorption of vapors of an organic nature, activated carbon has superior properties, having hydrocarbon-selective properties and high adsorption capacity for such materials. Inorganic adsorbents, such as activated alumina or silica gel, can also be used to adsorb organic materials, but difficulties can arise during regeneration. Activated alumina, silica gel, and molecular sieves will also preferentially adsorb any water vapor with the organic contaminant. At times this may be a considerable drawback in the application of these adsorbents for organic-contaminant removal.

The normal method of regeneration of adsorbents is by use of steam, inert gas (i.e., nitrogen), or other gas streams, and in the majority of cases this can cause at least slight decomposition of the organic compound on the adsorbent. Two difficulties arise: (1) incomplete recovery of the adsorbate, although this may be unimportant; and (2) progressive deterioration in capacity of the adsorbent as the number of cycles increases owing to blocking of the pores from carbon formed by hydrocarbon decomposition. With activated carbon, a steaming process is used, and the difficulties of regeneration are thereby overcome. This is not feasible with silica gel or activated alumina because of the risk of breakdown of these materials when in contact with liquid water.

In some cases, none of the adsorbents has sufficient retaining capacity for a particular contaminant. In these applications, a large-surface-area adsorbent can be impregnated with an inorganic compound or, in rare cases, with a high-molecular-weight organic compound that can react chemically with the particular contaminant. For example, iodine-impregnated carbons are used for removal of mercury vapor and bromine-impregnated carbons for ethylene or propylene removal. The action of these impregnants is either catalytic conversion or reaction to a nonobjectionable compound or to a more easily adsorbed compound. For this case, general adsorption theory no longer applies to the overall effects of the process. For example, mercury removal by an iodine-impregnated carbon proceeds faster at a higher temperature, and a better overall efficiency can be obtained than in a low-temperature system.

Since adsorption takes place at the interphase boundary, the adsorption surface area becomes an important consideration. Generally, the higher the adsorption surface area, the greater its adsorption capacity. However, the surface area has to be "available" in a particular pore size within the adsorbent. At low partial pressure (or concentration) a surface area in the smallest pores in which the adsorbate can enter is the most efficient. At higher pressures the larger pores become more important; at very high concentrations, capillary condensation will take place within the pores, and the total micropore volume becomes the limiting factor.

The action of molecular sieves is slightly different from that of other adsorbents in that selectivity is determined more by the pore-size limitations of the particular sieve. In selecting molecular sieves, it is important that the contaminant to be removed be smaller than the available pore size. Hence, it is important that the particular adsorbent not only have an affinity for the contaminant in question but also have sufficient surface area available for adsorption.

Design Data The adsorbent having been selected, the next step is to calculate the quantity of adsorbent required and eventually consider other factors such as the temperature rise of the gas stream due to adsorption and the useful life of the adsorbent under operating conditions. The sizing and overall design of the adsorption system depend on the properties and characteristics of both the feed gas to be treated and the adsorbent. The following information should be known or available for design purposes:

1. Gas stream
   a. Adsorbate concentration.
   b. Temperature.
   c. Temperature rise during adsorption.
   d. Pressure.
   e. Flow rate.
   f. Presence of adsorbent contaminant material.
2. Adsorbent
   a. Adsorption capacity as used on stream.
   b. Temperature rise during adsorption.
   c. Isothermal or adiabatic operation.
   d. Life, if presence of contaminant material is unavoidable.
   e. Possibility of catalytic effects causing an adverse chemical reaction in the gas stream or the formation of solid polymerizates on the adsorbent bed, with consequent deterioration.
   f. Bulk density.
   g. Particle size, usually reported as a mean equivalent particle diameter. The dimensions and shape of particles affect both the pressure drops through the adsorbent bed and the diffusion rate into the particles. All things being equal, adsorbent beds consisting of smaller particles, although causing a higher pressure drop, will be more efficient.
   h. Pore data, which are important because they may permit elimination from consideration of adsorbents whose pore diameter will not admit the desired adsorbate molecule.
   i. Hardness, which indicates the care that must be taken in handling adsorbents to prevent the formation of undesirable fines.
   j. Regeneration information.

The design techniques used include both stagewise and continuous-contacting methods and can be applied to batch, continuous, and semicontinuous operations.

Adsorption Phenomena The adsorption process involves three necessary steps. The fluid must first come in contact with the adsorbent, at which time the adsorbate is preferentially or selectively adsorbed on the adsorbent. Next the fluid must be separated from the adsorbent-adsorbate, and, finally, the adsorbent must be regenerated by removing the adsorbate or by discarding used adsorbent and replacing it with fresh material. Regeneration is performed in a variety of ways, depending on the nature of the adsorbate. Gases or vapors are usually desorbed by either raising the temperature (thermal cycle) or reducing the pressure (pressure cycle). The more popular thermal cycle is accomplished by passing hot gas through the adsorption bed in the direction opposite to the flow during the adsorption cycle. This ensures that the gas passing through the unit during the adsorption cycle always meets the most active adsorbent last and that the adsorbate concentration in the adsorbent at the outlet end of the unit is always maintained at a minimum.

In the first step, in which the molecules of the fluid come in contact with the adsorbent, an equilibrium is established between the adsorbed fluid and the fluid remaining in the fluid phase. Figures 25-7 through 25-9 show several experimental equilibrium adsorption isotherms for a number of components adsorbed on various adsorbents. Consider Fig. 25-7, in which the concentration of adsorbed gas on the solid is plotted against the equilibrium partial pressure p^0 of the vapor or gas at constant temperature. At 40° C, for example, pure propane vapor at a pressure of 550 mm Hg is in equilibrium with an adsorbate concentration at point P of 0.04 lb adsorbed propane per pound of silica gel. Increasing the pressure of the propane will cause

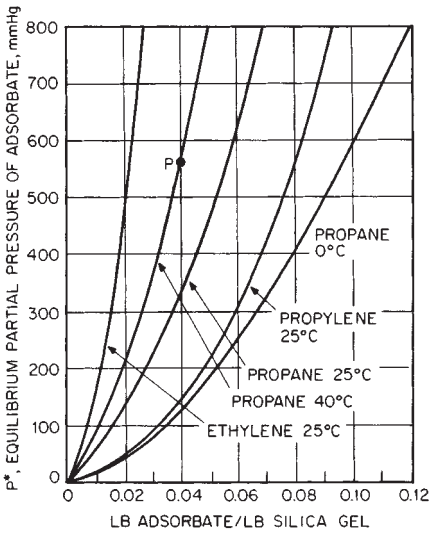


FIG. 25-7 Equilibrium partial pressures for certain organics on silica gel.

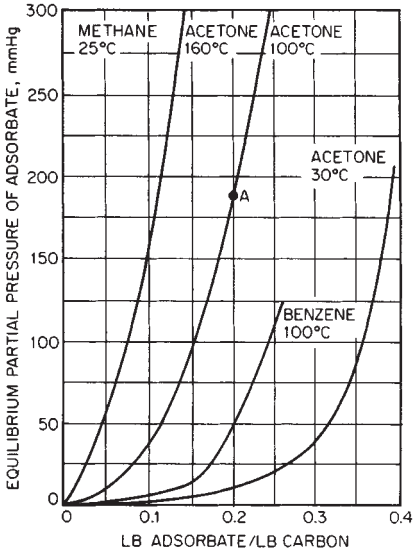


FIG. 25-8 Equilibrium partial pressures for certain organics on carbon.

more propane to be adsorbed, while decreasing the pressure of the system at *P* will cause propane to be desorbed from the carbon.

The adsorptive capacity of activated carbon for some common solvent vapors is shown in Table 25-27.

Adsorption-Control Equipment If a gas stream must be treated for a short period, usually only one adsorption unit is necessary, provided, of course, that a sufficient time interval is available between adsorption cycles to permit regeneration. However, this is usually not the case. Since an uninterrupted flow of treated gas is often required, it is necessary to employ one or more units capable of operating in this fashion. The units are designed to handle gas flows without interruption and are characterized by their mode of contact, either staged or continuous. By far the most common type of adsorption system used to remove an objectionable pollutant from a gas stream consists of a number of fixed-bed units operating in such a sequence that the gas flow remains uninterrupted. A two- or three-bed system is usually employed, with one or two beds bypassed for regeneration while one is adsorbing. A typical two-bed system is shown in Fig. 25-10, while a typical three-bed system is shown in Fig. 25-11. The type of system best suited for a particular job is determined from several factors, including the amount and rate of material being adsorbed, the time between cycles, the time required for regeneration, and the cooling time, if required.

Typical of continuous-contact operation for gaseous-pollutant adsorption is the use of a fluidized bed. During steady-state staged-contact operation, the gas flows up through a series of successive fluidized-bed stages, permitting maximum gas-solid contact on each stage. A typical arrangement of this type is shown in Fig. 25-12 for multistage countercurrent adsorption with regeneration. In the upper part of the tower, the particles are contacted countercurrently on perforated trays in relatively shallow beds with the gas stream containing the pollutant, the adsorbent solids moving form tray to tray through downspouts. In the lower part of the tower, the adsorbent is regenerated by similar contact with hot gas, which desorbs and carries off the pollutant. The regenerated adsorbent is then recirculated by an airlift to the top of the tower.

Although the continuous-countercurrent type of operation has found limited application in the removal of gaseous pollutants from process streams (for example, the removal of carbon dioxide and sulfur compounds such as hydrogen sulfide and carbonyl sulfide), by far the most common type of operation presently in use is the fixed-bed adsorber. The relatively high cost of continuously transporting solid particles as required in steady-state operations makes fixed-bed adsorption an attractive, economical alternative. If intermittent or batch operation is practical, a simple one-bed system, cycling alternately between the adsorption and regeneration phases, will suffice.

Additional information may be found by referring to the appropriate sections of this *handbook*. A comprehensive treatment of adsorber design principles is given in Buonicore and Theodore, *Industrial Control Equipment for Gaseous Pollutants*, vol. 1, 2d ed., CRC press, Boca Raton, Florida, 1992.

Combustion Many organic compounds released from manufacturing operations can be converted to innocuous carbon dioxide and water by rapid oxidation (chemical reaction): combustion. However, combustion of gases containing halides may require the addition of acid gas treatment to the combustor exhaust.

Three rapid oxidation methods are typically used to destroy combustible contaminants: (1) flares (direct-flame-combustion), (2) thermal combustors, and (3) catalytic combustors. The thermal and flare methods are characterized by the presence of a flame during combustion. The combustion process is also commonly referred to as "afterburning" or "incineration."

To achieve complete combustion (i.e., the combination of the combustible elements and compounds of a fuel with all the oxygen that they can utilize), sufficient space, time, and turbulence and a temperature high enough to ignite the constituents must be provided.

The three T's of combustion—time, temperature, and turbulence—govern the speed and completeness of the combustion reaction. For complete combustion, the oxygen must come into intimate contact with the combustible molecule at sufficient temperature and for a sufficient length of time for the reaction to be completed. Incomplete reactions may result in the generation of aldehydes, organic acids, carbon, and carbon monoxide.

Combustion-Control Equipment Combustion-control equipment can be divided into three types: (1) flares, (2) thermal incinerators, (3) catalytic incinerators.

Flares In many industrial operations and particularly in chemical plants and petroleum refineries, large volumes of combustible waste gases are produced. These gases result from undetected leaks in the operating equipment, from upset conditions in the normal operation of a plant in which gases must be vented to avoid dangerously high pressures in operating equipment, from plant startups, and from emergency shutdowns. Large quantities of gases may also result from off-specification product or from excess product that cannot be sold. Flows are typically intermittent, with flow rates during major upsets of up to several million cubic feet per hour.

The preferred control method for excess gases and vapors is to

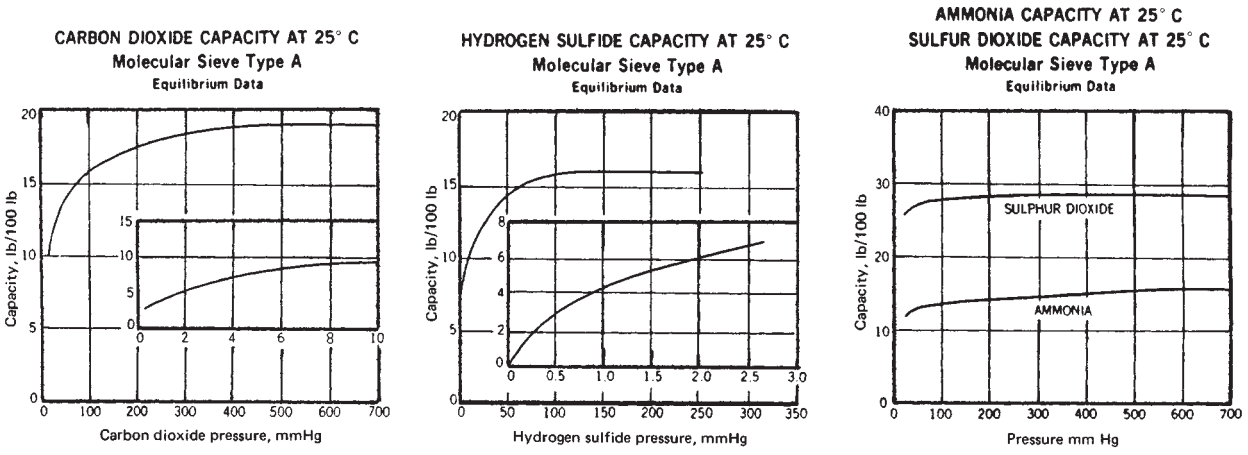


FIG. 25-9 Equilibrium partial pressures for certain gases on molecular sieves. (*A. J. Buonicore and L. Theodore,* Industrial Control Equipment for Gaseous Pollutants, *vol. I, CRC Press, Boca Raton, Fla., 1975.*)

recover them in a blowdown recovery system. However, large quantities of gas, especially those during upset and emergency conditions, are difficult to contain and reprocess. In the past all waste gases were vented directly to the atmosphere. However, widespread venting caused safety and environmental problems, and, in practice, it is now customary to collect such gases in a closed flare system and to burn them as they are discharged.

Although flares can be used to dispose of excess waste gases, such systems can present additional safety problems. These include the explosion potential, thermal-radiation hazards from the flame, and the problem of toxic asphyxiation during flameout. Aside from these safety aspects, there are several other problems associated with flaring that must be dealt with during the design and operation of a flare system. These problems include the formation of smoke, the luminosity of the flame, noise during flame, and the possible emission of by-product air pollutants during flaring.

The heat content of the waste stream to be disposed is another important consideration. The heat content of the waste gas falls into two classes. The gases can either support their own combustion or not. In general, a waste gas with a heating value greater than 7443 kJ/m^3 (200 Btu/ft^3) can be flared successfully. The heating value is based on the lower heating value of the waste gas at the flare. Below 7443 kJ/m^3, enriching the waste gas by injecting another gas with a higher heating value may be necessary. The addition of such a rich gas is called "endothermic flaring." Gases with a heating value as low as 2233 kJ/m^3 (60 Btu/ft^3) have been flared but at a significant fuel demand. It is usually not feasible to flare a gas with a heating value below 3721 kJ/m^3 (100 Btu/ft^3). If the flow of low-Btu gas is continuous, thermal or catalytic incineration can be used to dispose of the gas. For intermittent flows, however, endothermic flaring may be the only possibility.

TABLE 25-27 Adsorptive Capacity of Common Solvents on Activated Carbons*

Solvent	Carbon bed weight, %†
Acetone	8
Heptane	6
Isopropyl alcohol	8
Methylene chloride	10
Perchloroethylene	20
Stoddard solvent	2–7
1,1,1-Trichloroethane	12
Trichloroethylene	15
Trichlorotrifluoroethane	8
VM&P naphtha	7

*Assuming steam desorption at 5 to 10 psig.
†For example, 8 lb of acetone adsorbed on 100 lb of activated carbon.

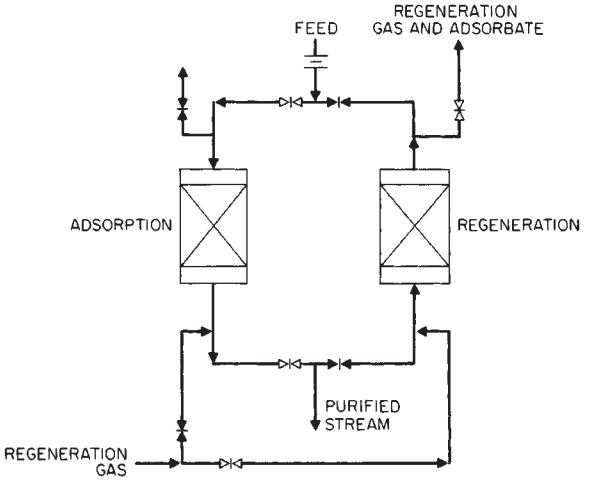


FIG. 25-10 Typical two-bed adsorption system.

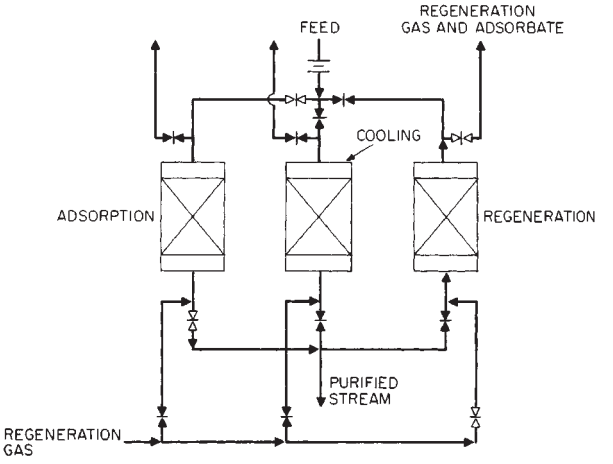


FIG. 25-11 Typical three-bed adsorption system.

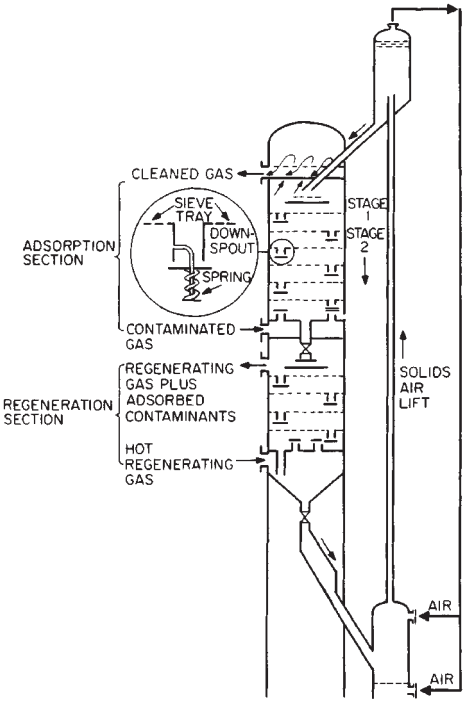


FIG. 25-12 Multistage countercurrent adsorption with regeneration.

Although most flares are used to dispose of intermittent waste gases, some continuous flares are in use, but generally only for relatively small volumes of gases. The heating value of large-volume continuous-flow waste gases is usually too valuable to lose in a flare. Vapor recovery or the use of the vapor as a fuel in a process heater is preferred over flaring. Since auxiliary fuel must be added to the gas in order to flare, large continuous flows of a low-heating-value gas are usually more efficient to burn in a thermal incinerator than in the flame of a flare.

Flares are mostly used for the disposal of hydrocarbons. Waste gases composed of natural gas, propane, ethylene, propylene, butadiene, and butane probably constitute over 95 percent of the material flared. Flares have been used successfully to control malodorous gases such as mercaptans and amines, but care must be taken when flaring these gases. Unless the flare is very efficient and gives good combustion, obnoxious fumes can escape unburned and cause a nuisance.

Flaring of hydrogen sulfide should be avoided because of its toxicity and low odor threshold. In addition, burning relatively small amounts of hydrogen sulfide can create enough sulfur dioxide to cause crop damage or a local nuisance. For gases whose combustion products may cause problems, such as those containing hydrogen sulfide or chlorinated hydrocarbons, flaring is not recommended.

Thermal Incinerators Thermal incinerators or afterburners can be used over a fairly wide but low range of organic vapor concentration. The concentration of the organics in air must be substantially below the lower flammable level (lower explosive limit). As a rule, a factor of four is employed for safety precautions. Reactions are conducted at elevated temperatures to ensure high chemical-reaction rates for the organics. To achieve this temperature, it is necessary to preheat the feed stream using auxiliary energy. Along with the contaminant-laden gas stream, air and fuel are continuously delivered to the incinerator (see Fig. 25-13). The fuel and contaminants are combusted with air in a firing unit (burner). The burner may utilize the air in the process-waste stream as the combustion air for the auxiliary fuel, or it may use a separate source of outside air. The products of combustion and the unreacted feed stream are intensely mixed and

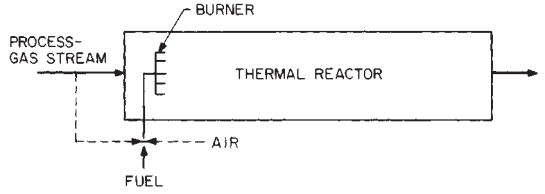


FIG. 25-13 Thermal-combustion device.

enter the reaction zone of the unit. The pollutants in the process-gas stream are then reacted at the elevated temperature. Thermal incinerators generally require operating temperatures in the range of 650 to 980° C (1200 to 1800° F) for combustion of most organic pollutants (see Table 25-28). A residence time of 0.2 to 1.0 is often recommended, but this factor is dictated primarily by complex kinetic considerations. The kinectics of hydrocarbon (HC) combustion in the presence of excess oxygen can be simplified into the following first-order rate equation:

$$\frac{d(HCl)}{dt} = -k[HCl] \tag{25-1}$$

where k = pseudo-first-order rate constant (s^{-1}). If the initial concentration is $C_{A,o}$, the solution of Eq. (25-1) is:

$$\ln\left(\frac{C_A}{C_{A,o}}\right) = -kt \tag{25-2}$$

Equation (25-2) is frequently used for a kinetic modeling of a burner using mole fractions in the range of 0.15 and 0.001 for oxygen and HC, respectively. The rate constant is generally of the following Arrhenius form:

$$k = Ae^{-E/RT} \tag{25-3}$$

where: A = pre-exponential factor, s- (see Table 2, *Air Pollution Engineering Manual,* Van Nostrand Reinhold, New York, 1992, p. 62)
E = activation energy, cal/gmol (see Table 2, *Air Pollution Engineering Manual,* Van Nostrand Reinhold, New York, 1992, p. 62)
R = universal gas constant, 1.987 cal/gmol °K
T = absolute temperature, °K

The referenced table for A and E is a summary of first-order HC combustion reactions.

TABLE 25-28 Thermal Afterburners: Conditions Required for Satisfactory Performance in Various Abatement Applications

Abatement category	Afterburner residence time, s	Temperature, °F
Hydrocarbon emissions: 90 + % destruction of HC	0.3–0.5	1100–1250*
Hydrocarbons + CO: 90 + % destruction of HC + CO	0.3–0.5	1250–1500
Odor		
50–90% destruction	0.3–0.5	1000–1200
90–99% destruction	0.3–0.5	1100–1300
99 + % destruction	0.3–0.5	1200–1500
Smokes and plumes		
White smoke (liquid mist)		
Plume abatement	0.3–0.5	800–1000†
90 + % destruction of HC + CO	0.3–0.5	1250–1500
Black smoke (soot and combustible particulates)	0.7–1.0	1400–2000

*Temperatures of 1400 to 1500°F (760 to 816°C) may be required if the hydrocarbon has a significant content of any of the following: methane, cellosolve, and substituted aromatics (e.g., toluene and xylenes).

†Operation for plume abatement only is not recommended, since this merely converts a visible hydrocarbon emission into an invisible one and frequently creates a new odor problem because of partial oxidation in the afterburner.

The end combustion products are continuously emitted at the outlet of the reactor. The average gas velocity can range from as low as 3 m/s (10 ft/s) to as high as 15 m/s (50 ft/s). These high velocities are required to prevent settling of particulates (if present) and to minimize the dangers of flashback and fire hazards. Space velocity calculations are given in the "Incinerator Design and Performance Equation" section.

The fuel is usually natural gas. The energy liberated by reaction may be directly recovered in the process or indirectly recovered by suitable external heat exchange (see Fig. 25-14).

Because of the high operating temperatures, the unit must be constructed of metals capable of withstanding this condition. Combustion devices are usually constructed with an outer steel shell that is lined with refractory material. Refractory-wall thickness is usually in the 0.05- to 0.23-m (2- to 9-in) range, depending upon temperature considerations.

Some of the advantages of the thermal incinerators are:

1. Removal of organic gases
2. Removal of submicrometer organic particles
3. Simplicity of construction
4. Small space requirements

Some of the disadvantages are:

1. High operating costs
2. Fire hazards
3. Flashback possibilities

Catalytic Incinerators Catalytic incinerators are an alternative to thermal incinerators. For simple reactions, the effect of the presence of a catalyst is to (1) increase the rate of the reaction, (2) permit the reaction to occur at a lower temperature, and (3) reduce the reactor volume.

In a typical catalytic incinerator for the combustion of organic vapors, the gas stream is delivered to the reactor continuously by a fan at a velocity in the range of 3 to 15 m/s (10 to 30 ft/s), but at a lower temperature, usually in the range of 350 to 425° C (650 to 800° F), than the thermal unit. (Design and performance equations used for calculating space velocities are given in the next section). The gases, which may or may not be preheated, pass through the catalyst bed, where the combustion reaction occurs. The combustion products, which again are made up of water vapor, carbon dioxide, inerts and unreacted vapors, are continuously discharged from the outlet at a higher temperature. Energy savings can again be effected by heat recovery from the exit stream.

Metals in the platinum family are recognized for their ability to promote combustion at low temperatures. Other catalysts include various oxides of copper, chromium, vanadium, nickel, and cobalt. These catalysts are subject to poisoning, particularly from halogens, halogen and sulfur compounds, zinc, arsenic, lead, mercury, and particulates. It is therefore important that catalyst surfaces be clean and active to ensure optimum performance.

Catalysts may be porous pellets, usually cylindrical or spherical in shape, ranging from 0.16 to 1.27 cm (1/16 to ½ in) in diameter. Small sizes are recommended, but the pressure drop through the reactor increases. Among other shapes are honeycombs, ribbons, and wire mesh. Since catalysis is a surface phenomenon, a physical property of these particles is that the internal pore surface is nearly infinitely greater than the outside surface.

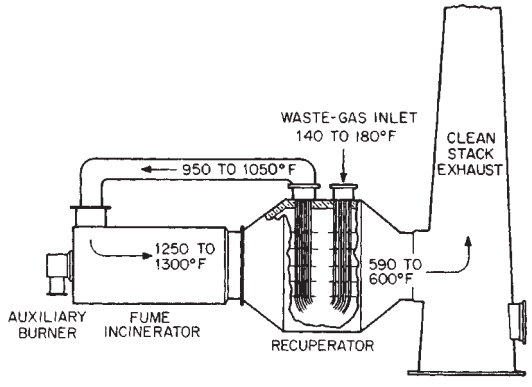


FIG. 25-14 Thermal combustion with energy (heat) recovery.

The following sequence of steps is involved in the catalytic conversion of reactants to products:

1. Transfer of reactants to and products from the outer catalyst surface
2. Diffusion of reactants and products within the pores of the catalyst
3. Activated adsorption of reactants and the desorption of the products on the active centers of the catalyst
4. Reaction or reactions on active centers on the catalyst surface

At the same time, energy effects arising from chemical reaction can result in the following:

1. Heat transfer to or from active centers to the catalyst-particle surface
2. Heat transfer to and from reactants and products within the catalyst particle
3. Heat transfer to and from moving streams in the reactor
4. Heat transfer from one catalyst particle to another within the reactor
5. Heat transfer to or from the walls of the reactor

Some of the advantages of catalytic incinerators are:

1. Lower fuel requirements as compared with thermal incinerators
2. Lower operating temperatures
3. Minimum insulation requirements
4. Reduced fire hazards
5. Reduced flashback problems

The disadvantages include:

1. Higher initial cost than thermal incinerators
2. Catalyst poisoning
3. Necessity of first removing large particulates
4. Catalyst-regeneration problems
5. Catalyst disposal

Incinerator Design and Performance Equations The key incinerator design and performance calculations are the required fuel usage and physical dimensions of the unit. The following is a general calculation procedure to use in solving for these two parameters, assuming that the process gas stream flow, inlet temperature, combustion temperature, and required residence time are known. The combustion temperature and residence time for thermal incinerators can be estimated using Table 25-28 and Eqs. (25-1) through (25-3).

1. The heat load needed to heat the inlet process gas stream to the incinerator operating temperature is:

$$Q = \Delta H \tag{25-4}$$

2. Correct the heat load for radiant heat losses, *RL*:

$$Q = (1 + RL)\,(\Delta H);\ RL = \text{fractionalbasis} \tag{25-5}$$

3. Assuming that natural gas is used to fire the burner with a known heating value of HV_G, calculate the available heat at the operating temperature. A shortcut method usually used for most engineering purposes is:

$$HA_T = (HV_G)\left(\frac{HA_T}{HV_G}\right)_{\text{ref}} \tag{25-6}$$

where the subscript "ref" refers to a reference fuel. For natural gas with a reference HV_G of 1059 Btu/scf, the heat from the combustion using no excess air would be given by:

$$(HA_T)_{\text{ref}} = -0.237(t) + 981;\ T = F \tag{25-7}$$

4. The amount of natural gas needed as fuel (*NG*) is given by:

$$NG = \frac{Q}{HA};\ \text{consistentunits} \tag{25-8}$$

5. The resulting volumetric flow rate is the sum of the combustion of the natural gas q and the process gas stream p at the operating temperature:

$$q_T = q_p + q_c \tag{25-9}$$

A good estimate for q_c is:

$$q_c = (11.5)(NG) \tag{25-10}$$

6. The diameter of the combustion device is given by:

$$S = \frac{q_T}{v_t} \tag{25-11}$$

where v_t is defined as the velocity of the gas stream at the incinerator operating temperature.

Condensation Frequently in air-pollution-control practice, it becomes necessary to treat an effluent stream consisting of a condensable pollutant vapor and a noncondensable gas. One control method to remove such pollutants from process-gas streams that is often overlooked is condensation. Condensers can be used to collect condensable emissions discharged to the atmosphere, particularly when the vapor concentration is high. This is usually accomplished by lowering the temperature of the gaseous stream, although an increase in pressure will produce the same result. The former approach is usually employed by industry, since pressure changes (even small ones) on large volumetric gas-flow rates are often economically prohibitive.

Condensation Equipment There are two basic types of condensers used for control: contact and surface. In contact condensers, the gaseous stream is brought into direct contact with a cooling medium so that the vapors condense and mix with the coolant (see Fig. 25-15). The more widely used system, however, is the surface condenser (or heat exchanger), in which the vapor and the cooling medium are separated by a wall (see Fig. 25-16). Since high removal efficiencies cannot be obtained with low-condensable vapor concentrations, condensers are typically used for pretreatment prior to some other more efficient control device such as an incinerator, absorber, or adsorber.

Contact Condensers Spray condensers, jet condensers, and barometric condensers all utilize water or some other liquid in direct contact with the vapor to be condensed. The temperature approach between the liquid and the vapor is very small, so the efficiency of the condenser is high, but large volumes of the liquid are necessary. If the vapor is soluble in the liquid, the system is essentially an absorptive one. If the vapor is not soluble, the system is a true condenser, in which case the temperature of the vapor must be below the dew point. Direct-contact condensers are seldom used for the removal of organic solvent vapors because the condensate will contain an organic-water mixture that must be separated or treated before disposal. They are, however, the most effective method of removing heat from hot gas streams when the recovery of organics is not a consideration.

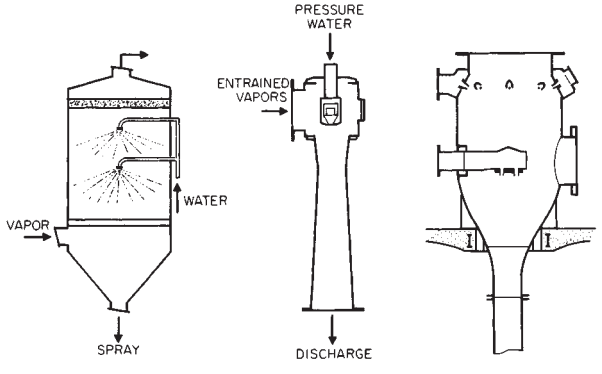


FIG. 25-15 Typical direct-contact condensers. (*a*) Spray chamber. (*b*) Jet. (*c*) Barometric.

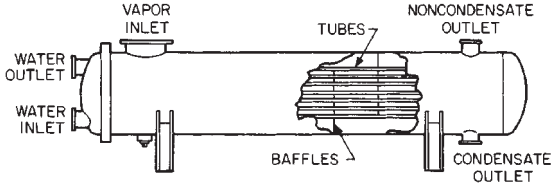


FIG. 25-16 Typical surface condenser (shell-and-tube).

In a direct-contact condenser, a stream of water or other cooling liquid is brought into direct contact with the vapor to be condensed. The liquid stream leaving the chamber contains the original cooling liquid plus the condensed substances. The gaseous stream leaving the chamber contains the noncondensable gases and such condensable vapor as did not condense; it is reasonable to assume that the vapors in the exit gas stream are saturated. It is then the temperature of the exit gas stream that determines the collection efficiency of the condenser.

The advantages of contact condensers are that (1) they can be used to produce a vacuum, thereby creating a draft to remove odorous vapors and also reduce boiling points in cookers and vats; (2) they usually are simpler and less expensive than the surface type; and (3) they usually have considerable odor-removing capacity because of the greater condensate dilution (13 lb of 60° F water is required to condense 1 lb of steam at 212° F and cool the condensate to 140° F). The principal disadvantage is the large water requirement. Depending on the nature of the condensate, odor in the wastewater can be offset by using treatment chemicals.

Direct-contact condensers involve the simultaneous transfer of heat and mass. Design procedures available for absorption, humidification, cooling towers, and the like may be applied with some modifications.

Surface Condensers Surface condensers (indirect-contact condensers) are used extensively in the chemical-process industry. They are employed in the air-pollution-equipment industry for recovery, control, and/or removal of trace impurities or contaminants. In the surface type, coolant does not contact the vapor condensate. There are various types of surface condensers including the shell-and-tube, fin-fan, finned-hairpin, finned-tube-section, and tubular. The use of surface condensers has several advantages. Salable condensate can be recovered. If water is used for coolant, it can be reused, or the condenser may be air-cooled when water is not available. Also, surface condensers require less water and produce 10 to 20 times less condensate. Their disadvantage is that they are usually more expensive and require more maintenance than the contact type.

Biofilters Biofilters are an APC technology that uses microorganisms, generally bacteria, to treat odorous off-gas emissions in an environmentally safe and economic manner. The biofilters consist of a porous filter media through which a waste gas stream is distributed. Microorganisms that feed on the waste gas are attached to this porous substrate. The biofiltration process is related to conventional activated sludge treatment in that, in both instances, the microorganisms are used to completely oxidize organic compounds into CO_2 and water. Biofilters are used to control the off-gas emissions from composting operations, rendering plants, food and tobacco processing, chemical manufacturing, iron and steel foundries, and other industrial facilities. Biofilters are in widespread use in Europe and Japan and are slowly becoming more acceptable as an APC technology in the United States.

General Process Description Biofilters are fixed film bioreactors that use microorganisms attached to substrate materials such as compost, peat, bark, soil, or inert materials to convert organic and inorganic waste products into CO_2 and water. The substrate provides structural support and elemental nutrients for the microbes. Its porous structure should provide adequate surface area at a reasonably low gas pressure drop. As waste gases are passed through the reactor, the target pollutants diffuse into the biofilm. The pollutants are then decomposed through the natural aerobic biodegradation process.

Biofilters are most economic when applied to low-concentration gas streams (<1000 ppm) that are also oxygen rich. Greater than 90 percent destruction efficiencies can be obtained for water-soluble organics such as alcohols, aldehydes, and amines. Water-soluble inor-

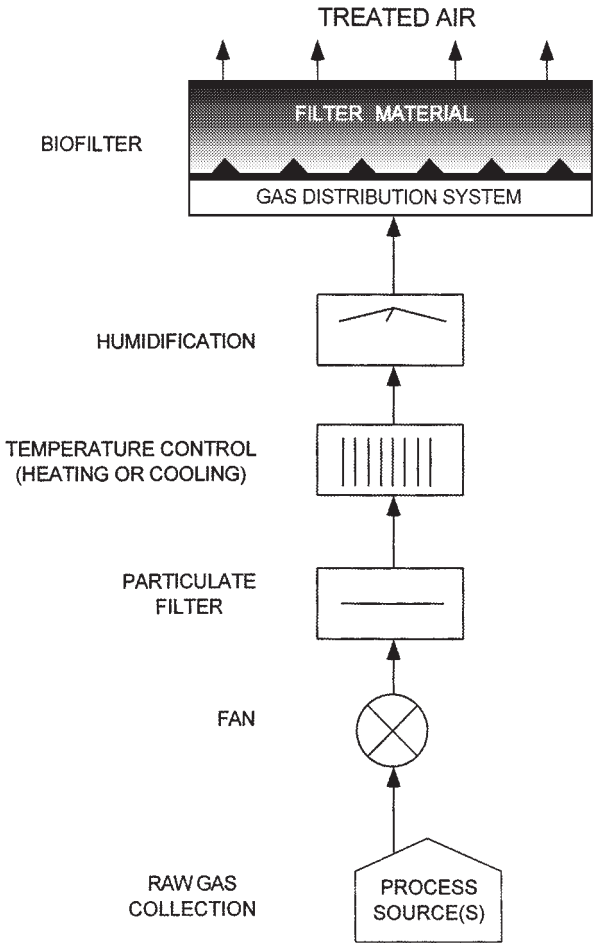


FIG. 25-17 Schematic flowsheet illustrating the individual elements of an open, single-layer biofilter system. Particulate filtration and/or temperature adjustment is often combined with the equipment to adjust gas humidity content.

ganics, such as H_2S and NH_3, can also readily undergo aerobic decomposition.

The basic biofilter process steps involved are shown in Fig. 25-17 and are as follows:

1. Collection and transportation of raw waste gases from the processing/manufacturing area to a gas pretreatment area via ductwork and blowers.
2. Pretreatment of the raw waste gas to remove particulates, adjust temperature and humidify to saturation.
3. The pretreated gas is evenly distributed throughout the biofilter.

Microorganisms The naturally occurring microorganisms that are commonly used in biofilters are the same bacteria and fungi that are currently used in activated-sludge wastewater treatment and landfills. Genetically engineered microbes have been created to digest manmade chemical species, such as the organic aromatics xylene and styrene. On-going genetic engineering research is expected to increase the number of chemical species that can be biodegraded. This will also contribute to lowering the cost and size of current filter beds by decreasing the required digestion time. The more commonly used microorganisms are listed in Table 25-29.

Design and Construction The capacity and efficiency of biofilter operation are a direct function of active surface area, filter void space, target removal efficiency, gas species, and gas loading. Proper design of the main biofilter components is very important to ensure a feasible, cost-effective operation.

TABLE 25-29 Microorganisms Frequently Identified in Biofilters

Bacteria	Fungi
Actinomyces globisporus	*Penicillium* spp.
Micrococcus albus	*Cephalosporium* spp.
Micromonospora vulgarus	*Mucor* spp.
Bacillus cereus	*Circinella* spp.
Streptomyces spp.	*Cephalotecium* spp.
	Ovularia spp.
	Stemphilium spp.

SOURCE: Data compiled from Ottengraf, S. P. P., "Biological Systems for Waste Gas Elimination," 1987, Table 3.

Raw Gas Composition The suitability of the raw gas stream must first be determined. The raw gas stream must contain the following in order to ensure both reasonable removal efficiencies and microorganism life expectancy:

1. An oxygen concentration equal to ambient level.
2. Gas concentrations below lethal levels for microorganisms used.
3. Lethal gas species must be absent from the raw gas stream.

Raw Gas Transport The gas is collected from the processing area and is transported by ductwork and ID fans to the preconditioning equipment.

Raw Gas Preconditioning In order to ensure the required destruction efficiency and continued biofilter life, the raw gas stream must be adjusted to a preselected range of particulate loading, temperature, and humidification before the gas can be safely introduced into the biofilter.

Preconditioning for Particulates Heavy particulate loading of the inlet gas with dust, grease, oils, or other aerosols can be very damaging to the pore structure of the filter bed, resulting in an eventual pressure-drop increase. Oils and heavy metals that are deposited on the filter bed can be poisonous to the microorganisms that live within the biofilm. Particulate APC equipment such as fabric filters and venturi scrubbers are generally adequate for this level of particulate removal.

Temperature The operating temperature of a biofilter is primarily controlled by the inlet gas temperature. The recommended operating temperature range for high destruction efficiency is between 20° to 40° C, with an optimum temperature of 37° C (98° F). At lower temperatures, the bacteria growth will be limited, and at extremely low temperatures the bacteria could possibly be destroyed. At temperatures above the recommended range, the bacteria's activity is also impaired. Extremely high temperatures will destroy the bacteria within the filter bed.

In terms of an economic determination, gas temperature adjustment is often the most important cost factor in determining whether to use a biofilter or a more conventional system. If the process gas stream is at an extremely high temperature (+100° C), the cost of cooling the inlet gas stream might favor more conventional methods for odor control such as thermal oxidation.

Humidification The microorganisms that digest the target pollutants live in a thin water layer called the biofilm that surrounds the filter substrate. Without the biofilm, the microorganisms would die; therefore, maintaining a wetted surface within the filter bed is crucial. Insufficient moisture can also lead to shrinking and cracking of the filter media, resulting in reduced active surface area and gas by-passing.

Humidification of the gas stream is the preferred method of keeping the filter bed moist. Gas moisture is usually added to the incoming gas stream downstream of the particulate removal APC equipment by either water sprays or steam. Adding moisture directly to the top of the bed in order to maintain filter media moisture is not recommended since this can result in: (1) localized drying of the substrate, and (2) cold water addition will reduce the activity of the microorganisms until the water becomes warmed to the steady-state filter-bed temperature.

Gas Distribution System The function of the gas distribution

system is to ensure even flow of the preconditioned gas stream to all areas of the filter bed. In upflow biofilter designs, the gas distribution system also provides the following:

1. A means of drainage, collection, and transportation of excess water within the filter bed
2. Prevents the potential contamination of surrounding soil by leaking filter leachate
3. A structural base for the filter bed media

The gas distribution system can be composed of a network of perforated pipe, slotted or vented concrete block, or metal grating. When there are no space limitations, single-level filters are used. In regions where footprint space is limited, like Japan, multiple-deck filter beds have become commonplace. If inorganic compounds are being treated, corrosion-resistant materials of construction are used due to the acidic by-products of the bioreaction.

Filter Matrix The most common filter substrates in use today are soils or compost produced from leaves, bark, wood chips, activated sludge, paper, or other organic materials. In selecting a proper filter substrate for a specific use, the following should be considered:

1. The particle size and porosity of the filter media, since operating efficiency is directly related to the available biofilm surface area.
2. The filter media must be a source of inorganic nutrients for the microbes. In cases of long-term operation, inorganic nutrients can be periodically added to the bed.
3. Compaction of the filter bed over time will result in gas channeling and pressure-drop increases. This can be avoided by adding large, rigid particles such as plastic spheres, ceramics, or wood/bark chips to provide additional support to the filter substrate.
4. Good bed drainage characteristics are necessary to ensure that reaction products are easily transported out of the filter media. The leachate is generally recycled through the humidification process to reduce the wastewater stream.
5. The filter media should have buffering capacity in order to maintain a pH of at least 3. This is especially a concern when inorganic compounds are targeted for reduction by the biofilter.
6. The filter media should be composed of materials that have a nonobjectional odor.

Kinetics The capacity and efficiency of biofilter operation is a function of active surface area, filter void space, target removal efficiency, gas species, gas concentration, and gas flow rate. A simplified theoretical model described by S.P.P. Ottengraf et al. is schematically represented by in Fig. 25-18. The mass balance made around the liquid-phase biolayer can be described as follows:

$$D \times \left(\frac{d^2C_1}{dx^2}\right) - R = 0 \qquad (25\text{-}12)$$

where: D = the mass-transfer coefficient, L^2/T
C_1 = liquid phase concentration, M/L^3
x = distance through biolayer, L
R = substrate utilization rate, $M/L^3/T$ (biodegradation rate)

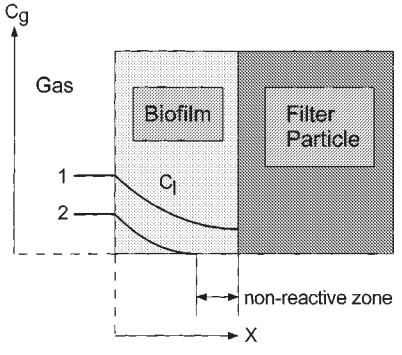


FIG. 25-18 Biophysical model for the biolayer. C_g is the concentration in the gas phase. The two concentration profiles shown in the biolayer (C_l) refer to (1) elimination reaction rate limited, and (2) diffusion limited. (SOURCE: Redrawn from Ref. 26.)

The Ottengraf biolayer mass balance assumes the following:

1. Monod kinetic model applies.
2. Biodegradation occurs in the biofilm liquid phase.
3. The biofilm thickness is small compared to the diameter of the substrate; therefore, the biofilm can be regarded as a flat surface.
4. Plug flow of the gas through the filter media.
5. Gas and liquid phase concentrations follow Henry's law.
6. Ideal gas law applies; i.e., no gas species interactions.
7. Steady state.

The biodegradation rate R is characterized by the Monod (or Michaelis-Menten) following relationship:

$$R = R_{\max} \times \frac{C_1}{(C_1 + K_m)} \qquad (25\text{-}13)$$

where: K_m = the Monod (Michaelis-Menten) constant, M/L^3
$R_{\max}$ = the maximum substrate utilization rate, $M/L^3/T$

$R_{\max}$ is a function of the active microorganism concentration in the biofilm and is defined as:

$$R_{\max} = X \times \frac{\mu_m}{y_i} \qquad (25\text{-}14)$$

where: X = cell concentration of the active microbes, M/L^3;
μ_m = the maximum growth rate of microbe species, $1/T$;
y_i = cell yield coefficient of microbe species, dimensionless

Two rate-limiting cases exist with the above mass balance:

1. *Reaction rate limited (zero-order kinetics).* In this case, the biofilm concentration has no effect on reaction rate, and the biodegradation breakthrough curve is linear.
2. *Diffusion rate limited (first-order kinetics).* In this case, the reaction rate is controlled by the rate of diffusion of the pollutant species into the biofilm.

The concentration profiles that result from the above two rate-controlling mechanisms are shown in Fig. 25-18.

One of the listed assumptions for Ottengraf's kinetic model was that no gas-phase interactions occur between different chemical species (the ideal-gas assumption). Under actual operating conditions, gas-phase interactions can either have a negative or positive impact on biofilter operation. These interactions include:

1. Cometabolism, which increases the biodegradation rate of the multiple targeted compounds.
2. Cross-inhibition, which decreases the biodegradation rate of the multiple targeted compounds.
3. Vertical stratification, where the most easily degraded compounds are metabolized first upon entering the filter bed. The more difficult-to-metabolize compounds pass through the lower region of the bed and are metabolized in the upper levels.

Based upon the above-mentioned species interactions, pilot-scale testing is generally recommended to accurately size a biofilter bed for a multicomponent waste gas stream.

Membrane Filtration Membrane systems have been used for several decades to separate colloidal and molecular slurries by the chemical process industries (CPI). Membrane filtration was not viewed as a commercially viable pollution control technology until recently. This conventional wisdom was due to fouling problems exhibited when handling process streams with high solid content. This changed with the advent of membranes composed of high-flux cellulose acetate. In Europe and Asia, membrane filtration systems have been used for several years, primarily for ethanol dewatering for synthetic fuel plants. Membrane systems were selected in these cases for their (1) low energy utilization; (2) modular design; (3) low capital costs; (4) low maintenance; and (5) superior separations. In the United States, as EPA regulations become increasingly stringent, a renewed interest in advanced membrane filtration systems has occurred. In this case, the driving factors are the membrane system's ability to operate in a pollution-free, closed-loop manner with minimum wastewater output. Low capital and maintenance costs also result from the small amount of moving parts within the membrane systems.

Process Descriptions Selectively permeable membranes have an increasingly wide range of uses and configurations as the need for

more advanced pollution control systems are required. There are four major types of membrane systems: (1) pervaporation; (2) reverse osmosis (RO); (3) gas absorption; and (4) gas adsorption. Only membrane pervaporation is currently commercialized.

Membrane Pervaporation Since 1987, membrane pervaporation has become widely accepted in the CPI as an effective means of separation and recovery of liquid-phase process streams. It is most commonly used to dehydrate liquid hydrocarbons to yield a high-purity ethanol, isopropanol, and ethylene glycol product. The method basically consists of a selectively-permeable membrane layer separating a liquid feed stream and a gas phase permeate stream as shown in Fig. 25-19. The permeation rate and selectivity is governed by the physicochemical composition of the membrane. Pervaporation differs from reverse osmosis systems in that the permeate rate is not a function of osmotic pressure, since the permeate is maintained at saturation pressure (Ref. 24).

Three general process groups are commonly used when describing pervaporation: (1) water removal from organics; (2) organic removal from water (solvent recovery); and (3) organic/organic separation. Organic/organic separations are very uncommon and therefore will not be discussed further.

Ethanol Dehydration The membrane-pervaporation process for dehydrating ethanol was first developed by GFT in West Germany in the mid 1970s, with the first commercial units being installed in Brazil and the Philippines. At both sites, the pervaporation unit was coupled to a continuous sugarcane fermentation process that produced ethanol at concentrations up to 96 percent after vacuum pervaporation. The key advantages of the GFT process are (1) no additive chemicals are required; (2) the process is skid-mounted (low capital costs and small footprint); (3) and there is a low energy demand. The low energy requirement is achieved because only a small fraction of the water is actually vaporized and that the required permeation driving force is provided by only a small vacuum pump. The basic ethanol dehydration process schematic is shown in Fig. 25-20. A key advantage of all pervaporation processes is that vapor-liquid equilibria and possible resulting azeotropic effects are irrelevant (see Fig. 25-21 and Ref. 24).

Solvent Recovery The largest current industrial use of pervaporation is the treatment of mixed organic process streams that have become contaminated with small (10 percent) quantities of water. Pervaporation becomes very attractive when dehydrating streams down to less than 1 percent water. The advantages result from the small operating costs relative to distillation and adsorption. Also, distillation is often impossible, since azeotropes commonly form in multicomponent organic/water mixtures.

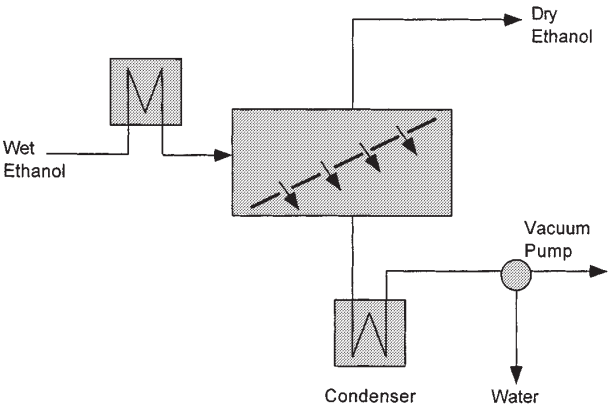


FIG. 25-20 Ethanol dehydration using pervaporation membrane. (SOURCE: Redrawn from Ref. 24.)

Pervaporation occurs in three basic steps:

1. Preferential sorption of chemical species
2. Diffusion of chemical species through the membrane
3. Desorption of chemical species from the membrane

Steps 1 and 2 are controlled by the specific polymer chemistry and its designed interaction with the liquid phase. The last step, consisting of evaporation of the chemical species, is considered to be a fast, nonselective process. Step 2 is the rate-limiting step. The development by the membrane manufacturers of highly selective, highly permeable composite membranes that resist fouling from solids has subsequently been the key to commercialization of pervaporation systems. The membrane composition and structure are designed in layers, with each layer fulfilling a specific requirement. Using membrane dehydration as an example, a membrane filter would be composed of a support layer of nonwoven porous polyester below a layer of polyacrylonitrile (PAN) or polysulfone ultrafiltration membrane and a layer of 0.1-μm-thick crosslinked polyacrylate, polyvinyl alcohol (PVA). Other separations membranes generally use the same two sublayers. The top layer is interchanged according to the selectivity desired.

Emerging Membrane Control Technologies The recent improvements in membrane technology have spawned several potentially commercial membrane filtration uses.

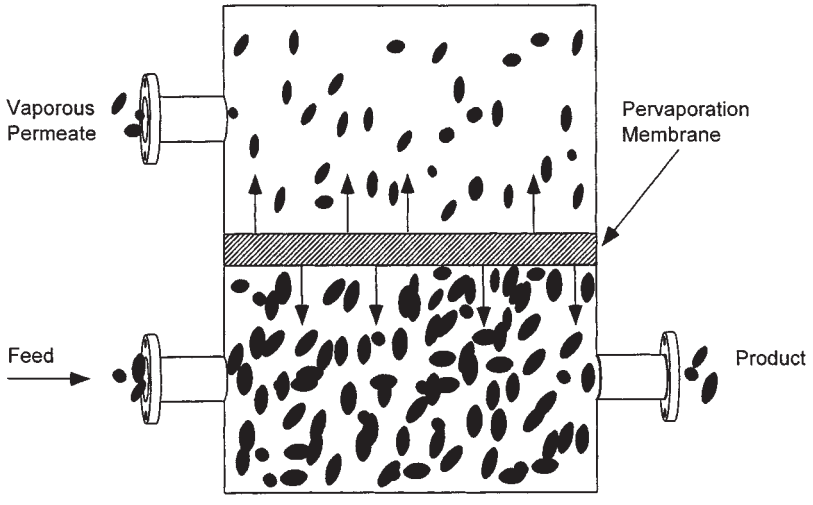


FIG. 25-19 Pervaporation of gas from liquid feed across membrane to vaporous permeate. (SOURCE: Redrawn from Ref. 24.)

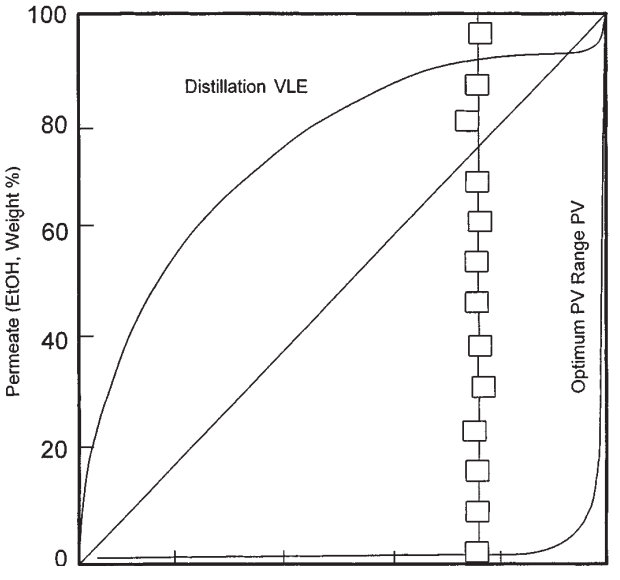


FIG. 25-21 Comparison of two types of pervaporation membranes to distillation of ethanol-water mixtures. (SOURCE: Redrawn from Ref. 24.)

Reverse Osmosis (RO) Membranes A type of membrane system for treating oily wastewater is currently undergoing commercialization by Bend Research, Inc. The system uses a tube-side feed module that yields high fluxes while being able to handle high-solids-content waste streams (Ref. 25). Another type of reverse osmosis technique is being designed to yield ultrapurified HF recovered from spent etching solutions. It is estimated that 20,000 tons of spent solution is annually generated in the United States and that using membrane RO could save 1 million bbl/yr of oil.

In Situ Filter Membranes In situ membranes are being fitted into incinerator flue-gas stacks in an attempt to reduce hydrocarbon emissions. Two types of commercially available gas separation membranes are being studied: (1) flat cellulose acetate sheets; and (2) hollow-tube fiber modules made of polyamides.

Vibratory Shear-Enhanced Membranes The vibratory shear-enhancing process (VSEP) is just starting commercialization by Logic International, Emeryville, CA. It employs the use of intense sinusiodal shear waves to ensure that the membrane surfaces remain active and clean of solid matter. The application of this technology would be in the purification of wastewater (Ref. 2).

Vapor Permeation Vapor permeation is similar to vapor pervaporation except that the feed stream for permeation is a gas. The future commercial viability of this process is based upon energy and capital costs savings derived from the feed already being in the vapor-phase, as in fractional distillation, so no additional heat input would be required. Its foreseen application areas would be the organics recovery from solvent-laden vapors and pollution treatment. One commercial unit was installed in Germany in 1989 (Ref. 26).

Selective Catalytic Reduction of Nitrogen Oxides The traditional approach to reducing ambient ozone concentrations has been to reduce VOC emissions, an ozone precurssor. In many areas, it has now been recognized that elimination of persistent exceedances of the National Ambient Air Quality Standard for ozone may require more attention to reductions in the other ingredients in ozone formation, nitrogen oxides (NO_x). In such areas, ozone concentrations are controlled by NO_x rather than VOC emissions.

Selective catalytic reduction (SCR) has been used to control NO_x emissions from utility boilers in Europe and Japan for over a decade. Applications of SCR to control process NO_x emissions in the chemical industry are becoming increasingly common. A typical SCR system is shown in Fig. 25-22.

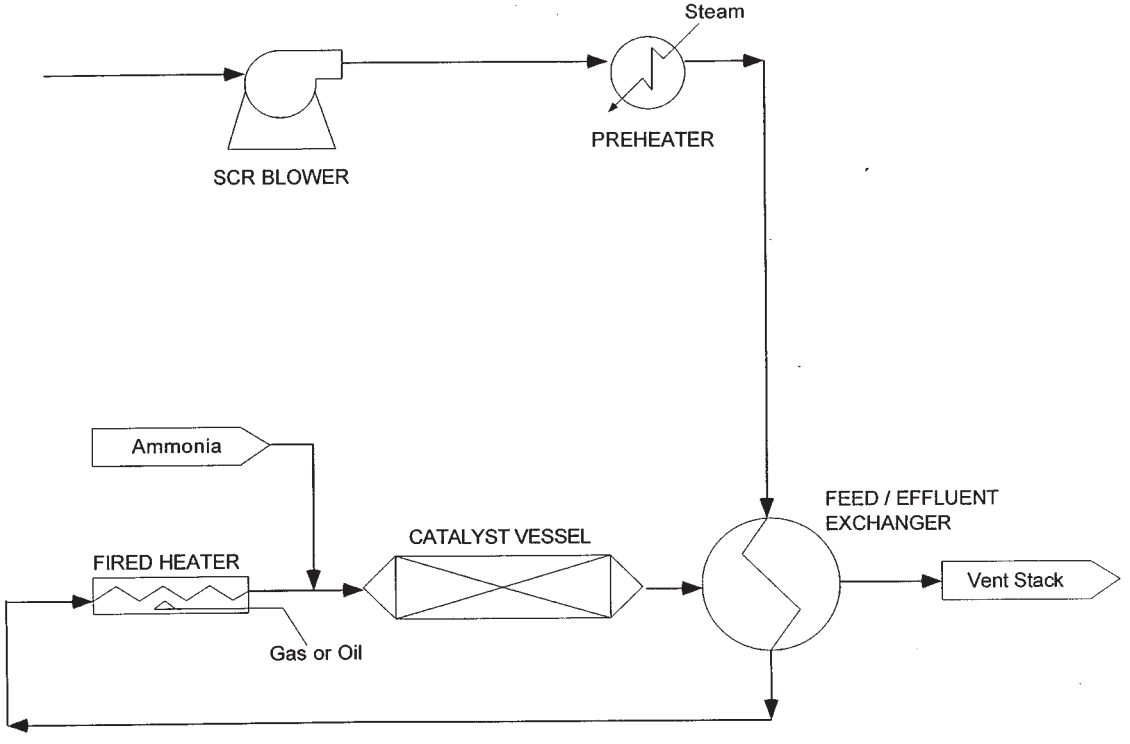


FIG. 25-22 Selective catalytic reduction of nitrogen oxides.

NO_x-laden fumes are preheated by effluent from the catalyst vessel in the feed/effluent heat exchanger and then heated by a gas- or oil-fired heater to over 600° F. A controlled quantity of ammonia is injected into the gas stream before it is passed through a metal oxide, zeolite, or promoted zeolite catalyst bed. The NO_x is reduced to nitrogen and water in the presence of ammonia in accordance with the following exothermic reactions:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$
$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$
$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

NO_x analyzers at the preheater inlet and catalyst vessel outlet monitor NO_x concentrations and control the ammonia feed rate. The effluent gives up much of its heat to the incoming gas in the feed/effluent exchanger. The vent gas is discharged at about 350° F.

SOURCE CONTROL OF PARTICULATE EMISSIONS

There are four conventional types of equipment used for the control of particulate emissions:

1. Mechanical collectors
2. Wet scrubbers
3. Electrostatic precipitators
4. Fabric filters

Each is discussed in Sec. 17 of this handbook under "Gas-Solids Separations." The effectiveness of conventional air-pollution-control equipment for particulate removal is compared in Fig. 25-23. These fractional efficiency curves indicate that the equipment is least efficient in removing particulates in the 0.1- to 1.0-μm range. For wet scrubbers and fabric filters, the very small particulates (0.1 μm) can be efficiently removed by brownian diffusion. The smaller the particulates, the more intense their brownian motion and the easier their collection by diffusion forces. Larger particulates (>1 μm) are collected principally by impaction, and removal efficiency increases with particulate size. The minimum in the fractional efficiency curve for scrubbers and filters occurs in the transition range between removal by brownian diffusion and removal by impaction.

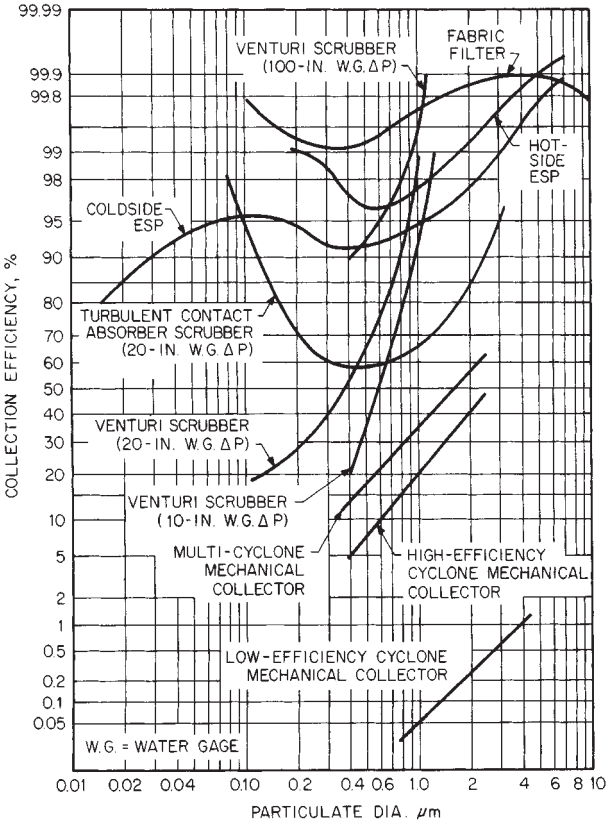


FIG. 25-23 Fractional efficiency curves for conventional air-pollution-control devices. [Chem. Eng., *87(13), 83 (June 30, 1980).*]

A somewhat similar situation exists for electrostatic precipitators. Particulates larger than about 1 μm have high mobilities because they are highly charged. Those smaller than a few tenths of a micrometer can achieve moderate mobilities with even a small charge because of aerodynamic slip. A minimum in collection efficiency usually occurs in the transition range between 0.1 and 1.0 μm. The situation is further complicated because not all particulates smaller than about 0.1 μm acquire charges in an ion field. Hence, the efficiency of removal of very small particulates decreases after reaching a maximum in the submicrometer range.

The selection of the optimum type of particulate collection device (i.e., ESP or fabric filter baghouse) is often not obvious without conducting a site-specific economic evaluation. This situation has been brought about by both the recent reductions in the allowable emissions levels and advancements with fabric filter and ESP technologies. Such technoeconomic evaluations can result in application and even site-specific differences in the final optimum choice (see *Precip Newsletter,* 220, June, 1994 and *Fabric Filter Newsletter,* 223, June, 1994).

Improvements in existing control technology for fine particulates and the development of advanced techniques are top-priority research goals. Conventional control devices have certain limitations. Precipitators, for example, are limited by the magnitude of charge on the particulate, the electric field, and dust reentrainment. Also, the resistivity of the particulate material may adversely affect both charge and electric field. Advances are needed to overcome resistivity and extend the performance of precipitators not limited by resistivity (see Buonicore and Theodore, "Control Technology for Fine Particulate Emissions," DOE Rep. ANL/ECT-5, Argonne National Laboratory, Argonne, Illinois, October 1978). Recent design developments with the potential to improve precipitator performance include pulse energization, electron beam ionization, wide plate spacing, and precharged units [Balakrishnan et al., "Emerging Technologies for Air Pollution Control," *Pollut. Eng.,* **11,** 28–32 (Nov. 1979); "Pulse Energization," *Environ. Sci. Technol.* **13**(9), 1044 (1974); and Midkaff, "Change in Precipitator Design Expected to Help Plants Meet Clean Air Laws," *Power,* **126**(10), 79 (1979)].

Fabric filters are limited by physical size and bag-life considerations. Some sacrifices in efficiency might be tolerated if higher air-cloth ratios could be achieved without reducing bag life (improved pulse-jet systems). Improvements in fabric filtration may also be possible by enhancing electrostatic effects that may contribute to rapid formation of a filter cake after cleaning.

Scrubber technology is limited by scaling and fouling, overall reliability, and energy consumption. The use of supplementary forces acting on particulates to cause them to grow or otherwise be more easily collected at lower pressure drops is being closely investigated. The development of electrostatic and flux-force-condensation scrubbers is a step in this direction.

The electrostatic effect can be incorporated into wet scrubbing by charging the particulates and/or the scrubbing-liquor droplets. Electrostatic scrubbers may be capable of achieving the same efficiency for fine-particulate removal as is achieved by high-energy scrubbers, but at substantially lower power input. The major drawbacks are increased maintenance of electrical equipment and higher capital cost.

Flux-force-condensation scrubbers combine the effects of flux force (diffusiophoresis and thermophoresis) and water-vapor condensation. These scrubbers contact hot, humid gas with subcooled liquid, and/or they inject steam into saturated gas, and they have demonstrated that a number of these novel devices can remove fine particulates (see Fig. 25-24). Although limited in terms of commercialization, these systems may find application in many industries.

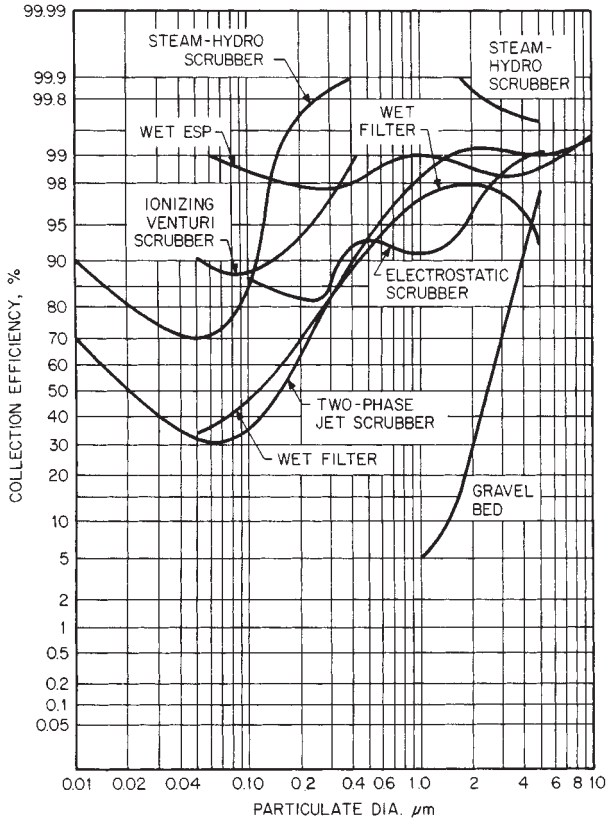


FIG. 25-24 Fractional efficiency curves for novel air-pollution-control devices. [Chem. Eng., **87***(13), 85 (June 30, 1980).*]

EMISSIONS MEASUREMENT

Introduction An accurate quantitative analysis of the discharge of pollutants from a process must be determined prior to the design and/or selection of control equipment. If the unit is properly engineered by utilizing the emission data as input to the control device and the code requirements as maximum-effluent limitations, most pollutants can be successfully controlled.

Sampling is the keystone of source analysis. Sampling methods and tools vary in their complexity according to the specific task; therefore, a degree of both technical knowledge and common sense is needed to design a sampling function. Sampling is done to measure quantities or concentrations of pollutants in effluent gas streams, to measure the efficiency of a pollution-abatement device, to guide the designer of pollution-control equipment and facilities, and/or to appraise contamination from a process or a source. A complete measurement requires a determination of the concentration and contaminant characteristics as well as the associated gas flow. Most statutory limitations require mass rates of emissions; both concentration and volumetric-flow-rate data are therefore required.

The selection of a sampling site and the number of sampling points required are based on attempts to get representative samples. To accomplish this, the sampling site should be at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance, such as a bend, expansion, contraction, valve, fitting, or visible flame.

Once the sampling location has been decided on, the flue cross section is laid out in a number of equal areas, the center of each being the point where the measurement is to be taken. For rectangular stacks, the cross section is divided into equal areas of the same shape, and the traverse points are located at the center of each equal area, as shown in Fig. 25-25. The ratio of length to width of each elemental area should be selected. For circular stacks, the cross section is divided into equal annular areas, and the traverse points are located at the centroid of each area. The location of the traverse points as a percentage of diameter from the inside wall to the traverse point for circular-stack sampling is given in Table 25-30. The number of traverse points necessary on each of two perpendiculars for a particular stack may be estimated from Fig. 25-26.

Once these traverse points have been determined, velocity measurements are made to determine gas flow. The stack-gas velocity is usually determined by means of a pitot tube and differential-pressure gauge. When velocities are very low (less than 3 m/s [10 ft/s]) and when great accuracy is not required, an anemometer may be used. For gases moving in small pipes at relatively high velocities or pressures, orifice-disk meters or venturi meters may be used. These are valuable as continuous or permanent measuring devices.

Once a flow profile has been established, sampling strategy can be considered. Since sampling collection can be simplified and greatly reduced depending on flow characteristics, it is best to complete the flow-profile measurement before sampling or measuring pollutant concentrations.

Sampling Methodology The following subsections review the methods specified for sampling commonly regulated pollutants as well as sampling for more exotic volatile and semivolatile organic compounds. In all sampling procedures, the main concern is to obtain a representative sample; the U.S. EPA has published reference sampling methods for measuring emissions of specific pollutants so that uniform procedures can be applied in testing to obtain a representative sample. Table 25-31 provides an overview of the regulatory citation for selected test methods. The test methods reviewed in the following subsections address measuring the emissions of the following pollutants: particulate matter, sulfur dioxide, nitrogen oxides, carbon monoxide, fluorides, hydrogen chloride, total gaseous organics, multiple metals, volatile organic compounds, and semivolatile organic compounds.

Each sampling method requires the use of complex sampling equipment that must be calibrated and operated in accordance with specified reference methods. Additionally, the process or source that is being tested must be operated in a specific manner, usually at rated capacity, under normal procedures.

Velocity and Volumetric Flow Rate The U.S. EPA has published Method 2 as a reference method for determining stack-gas velocity and volumetric flow rate. At several designated sampling points, which represent equal portions of the stack volume (areas in the stack), the velocity and temperature are measured with instrumentation shown in Fig. 25-27.

Measurements to determine volumetric flow rate usually require approximately 30 min. Since sampling rates depend on stack-gas velocity, a preliminary velocity check is usually made prior to testing for pollutants to aid in selecting the proper equipment and in determining the approximate sampling rate for the test.

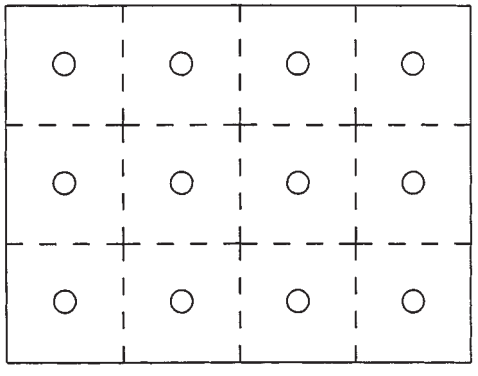
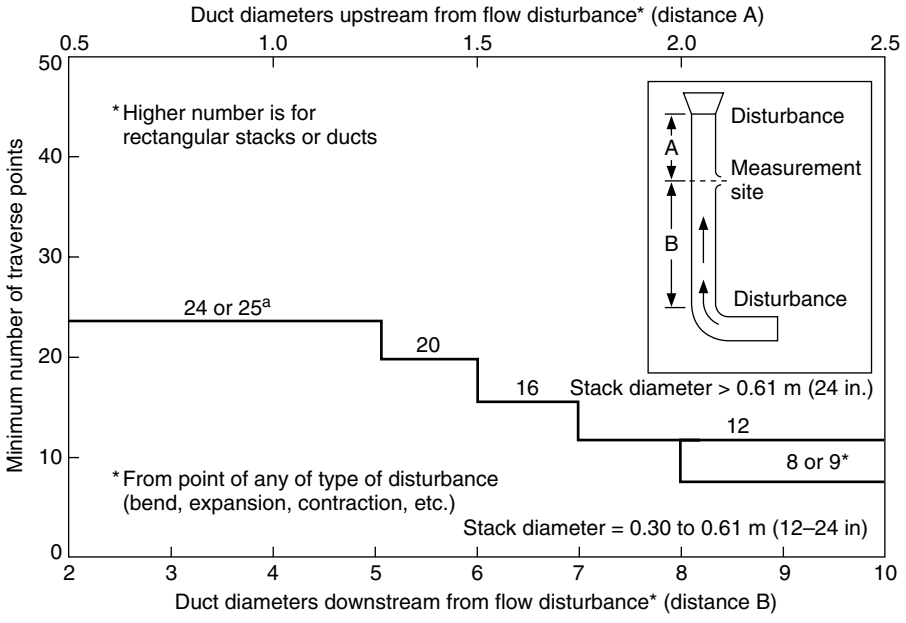
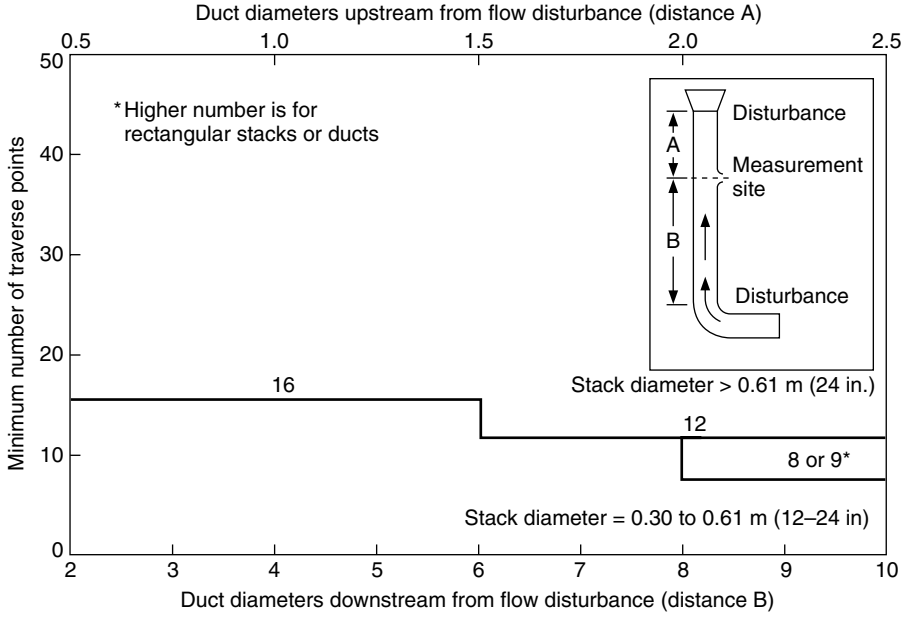


FIG. 25-25 Example showing rectangular stack cross section divided into 12 equal areas, with a traverse point at centroid of each area.



(a)

FIG. 25-26*a* Minimum number of traverse points for particulate traverses.



(b)

FIG. 25-26*b* Minimum number of traverse points for velocity (nonparticulate) traverse.

The volumetric flow rate determined by this method is usually within ±10 percent of the true volumetric flow rate.

Molecular Weight EPA Method 3 is used to determine carbon dioxide and oxygen concentrations and dry molecular weight of the stack-gas stream. Depending on the intended use of the data, these values can be obtained with an integrated sample (see Fig. 25-28) or a grab sample (see Fig. 25-29). In addition, the instrumental analyzer method, EPA Method 3A, is used for gas compositional analyses (O_2 and CO_2) in determining the sample gas molecular weight.

With the grab sampling technique, a sampling probe is placed at the center of the stack, and a sample is drawn directly into an Orsat analyzer or a Fyrite-type combustion-gas analyzer. The sample is then analyzed for carbon dioxide and oxygen content. With these data, the dry molecular weight of the gas stream can then be calculated.

TABLE 25-30 Location of Traverse Points in Circular Stacks

(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter										
	2	4	6	8	10	12	14	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	61.8	38.8	31.5	27.2
11						93.3	85.4	70.4	61.2	39.3	32.3
12						97.9	90.1	76.4	69.4	60.7	39.8
13							94.3	81.2	75.0	68.5	60.2
14							98.2	85.4	79.6	73.8	67.7
15								89.1	83.5	78.5	72.8
16								92.5	87.1	82.0	77.0
17								95.6	90.3	85.4	80.8
18								98.6	93.3	88.4	83.9
19									96.1	91.3	86.8
20									96.7	94.0	89.5
21										96.5	92.1
22										98.9	94.5
23											96.8
24											96.9

TABLE 25-31 Regulatory Citations for Selected Test Methods

Citation	Description	Selected methods included	Test parameter(s)
40 CFR Part 60 (Appendix A)	New source performance standards	Methods 1–4	Test location, volumetric flow rate, gas composition, moisture content
		Method 5	Particulate matter
		Method 6/6C	Sulfur dioxide
		Method 7/7E	Nitrogen oxides
		Method 9	Opacity of visible emissions
		Method 10	Carbon monoxide
		Method 13A or 13B	Total fluoride
		Method 23	Dioxins and furans
		Method 25/25A	Total gaseous non-methane organics (VOCs)
		Method 26/26A	Halogens, halides (primarily HCl, HF, Cl_2)
40 CFR Part 51 (Appendix M)	State implementation plans	Method 201A	Particulate matter of less than or equal to 10 μg (PM10)
40 CFR Part 266 (Appendix IX)	Boiler and industrial furnace (BIF) regulations	"Multiple metals"*	Cr, Cd, As, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, Hg
		Method Cr+6	Hexavalent chromium
		Method 0050	Isokinetic HCl/Cl_2
40 CFR Part 61 (Appendix B)	NESHAP regulations	Method 101A	Mercury
		Method 104	Beryllium
		Method 108	Arsenic
SW-846†		Method 0010	Semivolatile organics
		Method 0030	Volatile organics

NOTES:
*The multiple metals method is also currently published as Draft EPA Method 29 for inclusion in 40 CFR 60.
†Full citation is: *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods,* SW-846, 3d ed., July 1992.

The instrumental analyzer procedure, EPA Method 3A, is commonly used for the determination of oxygen and carbon dioxide concentrations in emissions from stationary sources. An integrated continuous gas sample is extracted from the test location and a portion of the sample is conveyed to one or more instrumental analyzers for determination of O_2 and CO_2 gas concentrations (see Fig. 25-30). The sample gas is conditioned prior to introduction to the gas analyzer by removing particulate matter and moisture. Sampling is conducted at a constant rate for the entire test run. Performance specifications and test procedures are provided in the method to ensure reliable data.

Moisture Content EPA Method 4 is the reference method for determining the moisture content of the stack gas. A value for moisture content is needed in some of the calculations for determining pollution-emission rates.

A sample is taken at several designated points in the stack, which represent equal areas. The sampling probe is placed at each sampling point, and the apparatus is adjusted to take a sample at a constant rate. As the gas passes through the apparatus, a filter collects the particulate matter, the moisture is removed, and the sample volume is measured. The collected moisture is then measured, and the moisture content of the gas stream is calculated. A schematic of the sampling used in this reference method is shown in Fig. 25-31.

Particulates Procedures for testing a particulate source are more detailed than those used for sampling gases. Because particulates exhibit inertial effects and are not uniformly distributed within a stack, sampling to obtain a representative sample is more complex than for gaseous pollutants. EPA Method 5 (as shown in Fig. 25-32) is the most widely used procedure for determination of particulate emissions from a stationary source. In-stack sampling guidelines are presented in EPA Method 17.

According to Method 5 (except as applied to fossil-fuel-fired steam generators), a particulate is defined as any material collected at

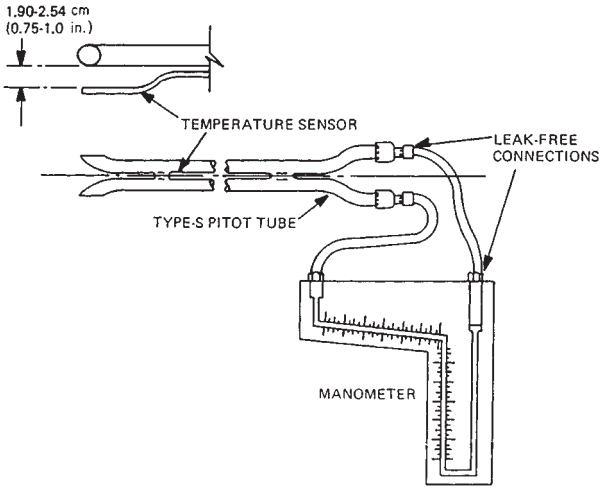


FIG. 25-27 Velocity-measurement system.

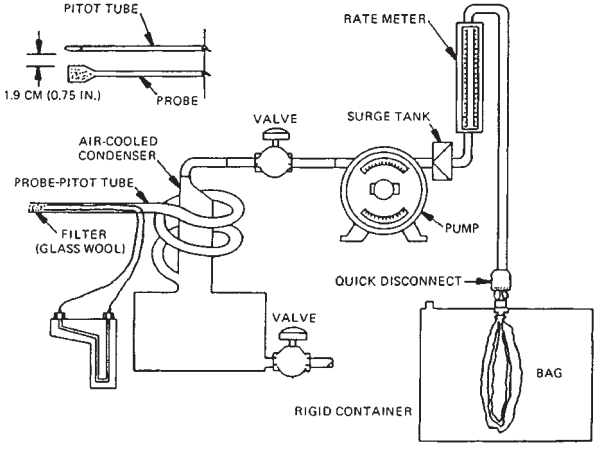


FIG. 25-28 Integrated-sample setup for molecular-weight determination.

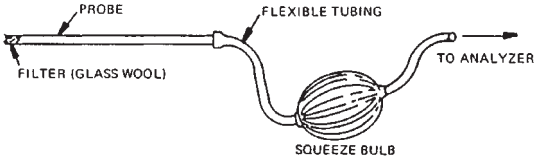


FIG. 25-29 Grab-sample setup for molecular-weight determination.

121° C (250° F) on a filtering medium. The sampling apparatus, however, may have to be modified to conform with the state's definition of a particulate. For example, a state may define *particulate* as any material collectible at stack conditions, a definition that would allow the filtering medium to be located in the stack.

In performing a particulate source test, samples are taken at several designated sampling points in the stack, which represent equal areas. At each sampling point, the velocity, temperature, molecular weight, and static pressure of the particulate-laden gas stream are measured. The sampling probe is placed at the first sampling point, and the sampling apparatus is adjusted to take a sample at the conditions measured at this point, and the process is repeated continuously until a sample has been taken from each designated sampling point. To achieve valid results in a particulate-source test, the sample must be taken isokinetically. Measurement of stack conditions allows adjustment of the sampling rate to meet this requirement.

As the gas stream proceeds through the sampling apparatus, the particulate matter is trapped on a filter, the moisture is removed, and the volume of the sample is measured. Upon completion of sampling, the collected material is recovered and sent to a laboratory for a gravimetric determination or analysis.

Sulfur Dioxide EPA Method 6 is the reference method for determining emissions of sulfur dioxide (SO_2) from stationary sources. As the gas goes through the sampling apparatus (see Fig. 25-33), the sulfuric acid mist and sulfur trioxide are removed, the SO_2 is removed by a chemical reaction with a hydrogen peroxide solution, and, finally, the sample gas volume is measured. Upon completion of the run, the sulfuric acid mist and sulfur trioxide are discarded, and the collected material containing the SO_2 is recovered for analysis at the laboratory. The concentration of SO_2 in the sample is determined by a titration method.

For determination of the total mass-emission rate of SO_2, the moisture content and the volumetric flow rate of the exhaust gas stream must also be measured.

The minimum detectable limit has been determined to be 3.4 mg of SO_2 per cubic meter of gas (2.1×10^{-7} lb of SO_2 per cubic foot of gas). Although no upper limit has been established, the theoretical upper concentration limit in a 20-liter sample is about 93,300 mg/m^3.

EPA Method 6C is the instrumental analyzer procedure used to determine sulfur dioxide emissions from stationary sources (see Fig. 25-30). An integrated continuous gas sample is extracted from the test location, and a portion of the sample is conveyed to an instrumental analyzer for determination of SO_2 gas concentration using an ultraviolet (UV), nondispersive infrared (NDIR), or fluorescence analyzer. The sample gas is conditioned prior to introduction to the gas analyzer by removing particulate matter and moisture. Sampling is conducted at a constant rate for the entire test run.

Quality control elements required by the instrumental analyzer method include: analyzer calibration error (±2 percent of instrument span allowed); verifying the absence of bias introduced by the sampling system (less than ±5 percent of span for zero and upscale calibration gases); and verification of zero and calibration drift over the test period (less than ±3 percent of span of the period of each run).

The analytical range is determined by the instrumental design. For this method, a portion of the analytical range is selected by choosing the span of the monitoring system. The span of the monitoring system is selected such that the pollutant gas concentration equivalent to the emission standard is not less than 30 percent of the span. If at any time during a run the measured gas concentration exceeds the span, the run is considered invalid.

The minimum detectable limit depends on the analytical range, span, and signal-to-noise ratio of the measurement system. For a well-designed system, the minimum detectable limit should be less than 2 percent of the span.

Nitrogen Oxides (NO_x) EPA Method 7 is the reference method for determining emissions of nitrogen oxides from stationary sources. Sampling for NO_x by this method is relatively simple with the proper equipment.

A sampling probe is placed at any location in the stack, and a grab sample is collected in an evacuated flask. This flask contains a solution of sulfuric acid and hydrogen peroxide, which reacts with the NO_x. The volume and moisture content of the exhaust-gas stream must be determined for calculation of the total mass-emission rate. The sample is sent to a laboratory, where the concentration of nitrogen oxides, except nitrous oxide, is determined colorimetrically.

Each grab sample is obtained fairly rapidly (15 to 30 s), and four grab samples constitute one run; a total of 12 grab samples is required for a complete series of three runs. An interval of 15 min between grab samples is required. The range of this method has been determined to be 2 to 400 mg of NO_x (as NO_2) per dry standard cubic meter (without dilution). Figure 25-34 shows a schematic of the sampling apparatus for an NO_x source test.

EPA Method 7E is the instrumental analyzer procedure used to

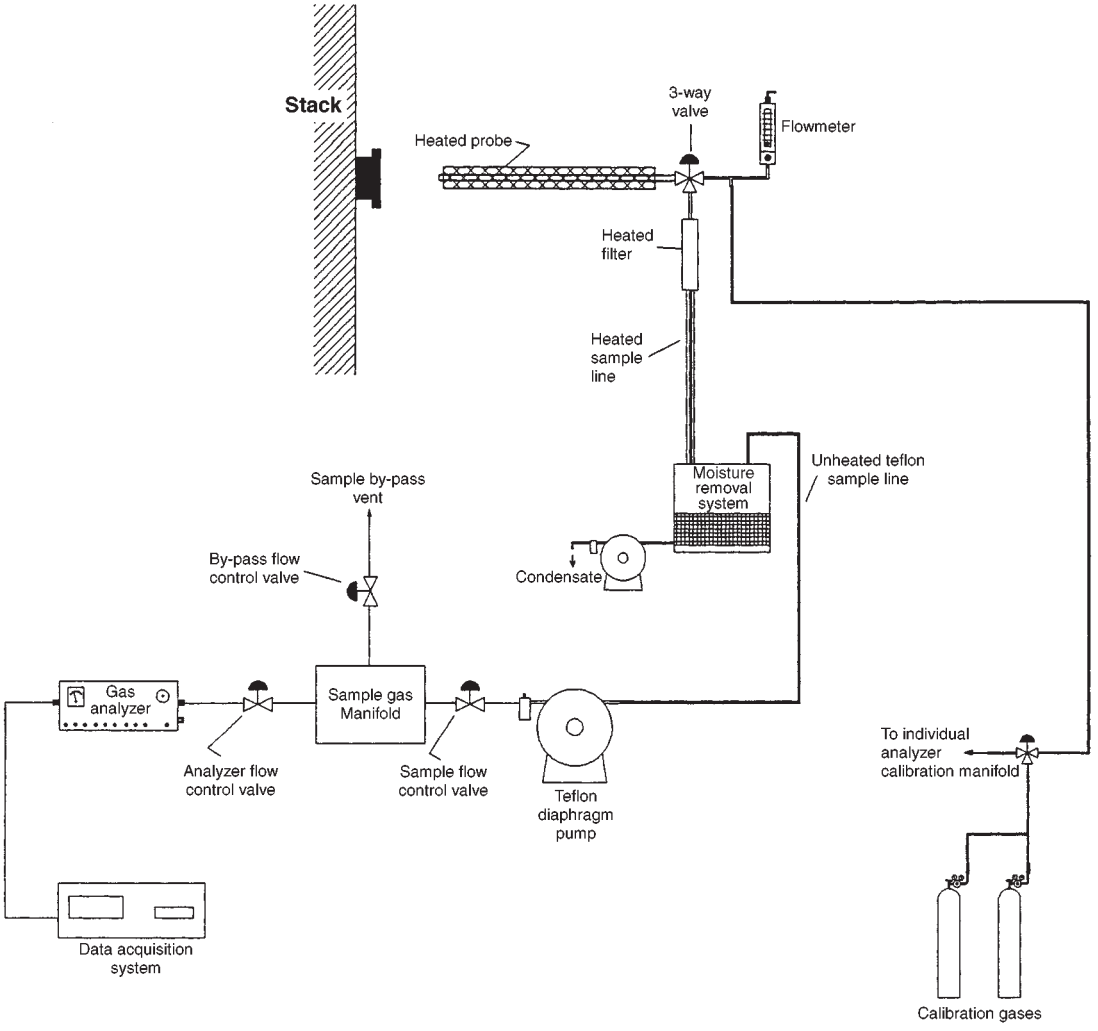


FIG. 25-30 Measurement system schematic for continuous emissions sampling (EPA Method 3A, 6C, or 7E).

determine NO_x emissions from stationary sources (see Fig. 26-28). An integrated continuous gas sample is extracted from the test location, and a portion of the sample is conveyed to an instrumental chemiluminescent analyzer for determination of NO_x gas concentration. The sample gas is conditioned prior to introduction to the gas analyzer by removing particulate matter and moisture. Sampling is conducted at a constant rate for the entire test run.

The NO_x analyzer is based on the principles of chemiluminescence to determine continuously the NO_x concentration in the sample gas stream. The analyzer should contain a NO_2-to-NO converter, which converts the nitrogen dioxide (NO_2) in the sample gas to nitrogen oxide (NO). An NO_2-to-NO converter is not necessary if data are presented to demonstrate that the NO_2 portion of the exhaust gas is less than 5 percent of the total NO_2 concentration.

Quality control elements required by the instrumental analyzer method include: analyzer calibration error (±2 percent of instrument span allowed); verifying the absence of bias introduced by the sampling system (less than ±5 percent of span for zero and upscale calibration gases); verification of zero and calibration drift over the test period (less than ±3 percent of span of the period of each run).

Carbon Monoxide (CO) EPA Method 10 is the reference method for determining emissions of carbon monoxide from stationary sources. An integrated or a continuous gas sample may be required, depending on operating conditions.

When the operating conditions are uniform and steady (there are no fluctuations in flow rate or in concentration of CO in the gas stream), the continuous sampling method can be used. A sampling probe is placed in the stack at any location, preferably near the center. The sample is extracted at a constant sampling rate. As the gas stream passes through the sampling apparatus, any moisture or carbon dioxide in the sample gas stream is removed. The CO concentration is then measured by a nondispersive infrared analyzer, which gives direct readouts of CO concentrations.

Figure 25-35 is a schematic of an assembled sampling apparatus used to determine CO concentrations by the continuous sampling method.

For an integrated sample, the sampling probe is located at any point near the center of the stack, and the sampling rate is adjusted proportionately to the stack-gas velocity. As the stack gas passes through the sampling apparatus, moisture is removed and the sample gas is collected in a flexible bag. Analysis of the sample is then performed in a laboratory with a nondispersive infrared analyzer. Figure 25-36 is a schematic of an assembled apparatus for the integrated sampling of CO.

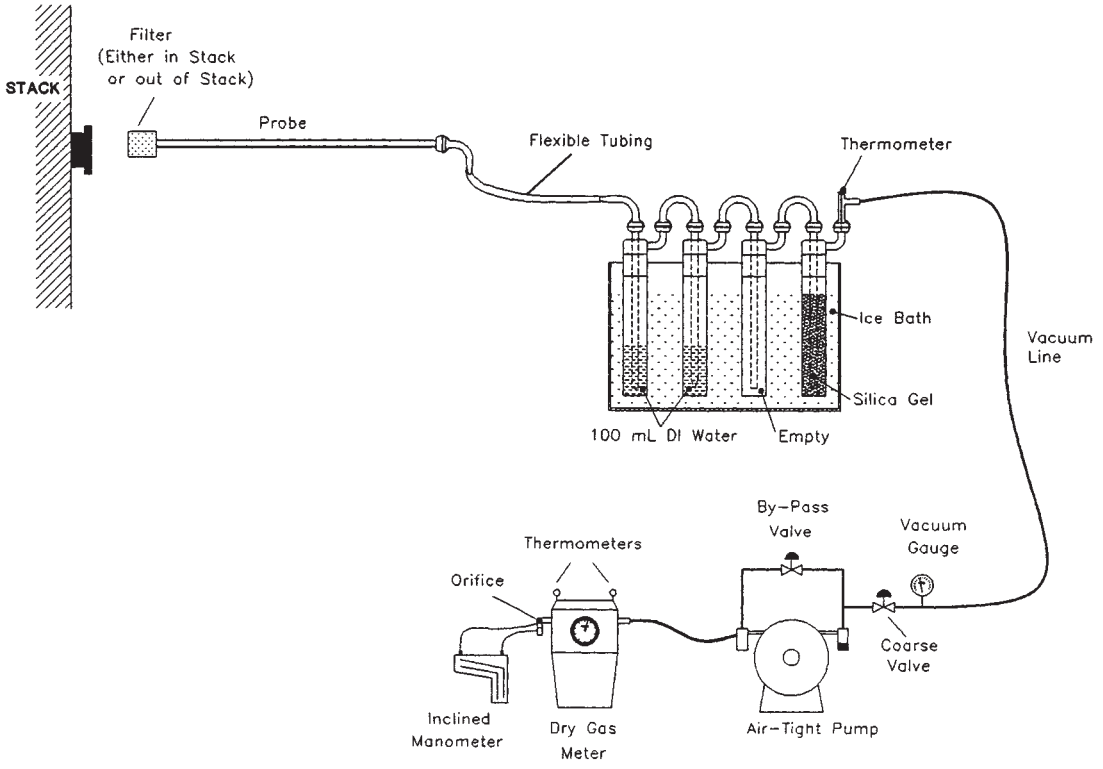


FIG. 25-31 EPA Method 4: moisture sampling train.

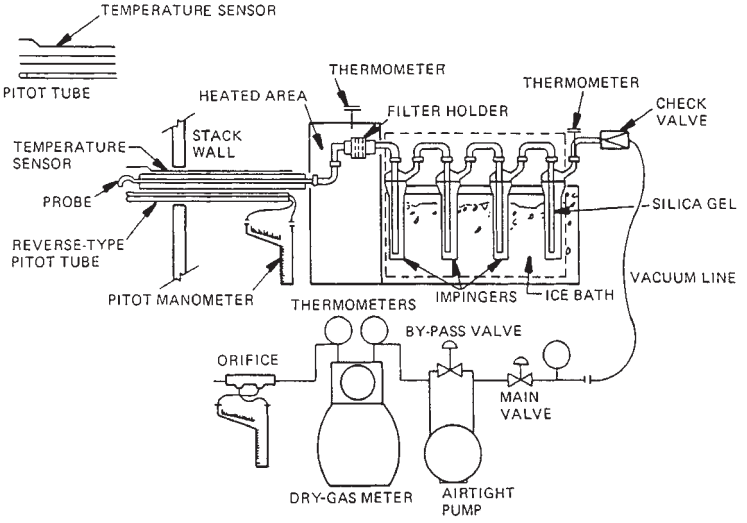


FIG. 25-32 EPA Method 5 particulate-sample apparatus.

A one-hour sampling period is generally required for this method. Sampling periods are specified by the applicable standard; e.g., standards for petroleum refineries require sampling for one hour or more.

For Method 10, the minimum detectable concentration of CO has been determined to be 20 ppm in a range of 1 to 1000 ppm.

Fluorides Two EPA reference methods, Method 13A and Method 13B, can be used to determine total fluoride emissions from a stationary source. The difference in the two methods is the analytical procedure for determining total fluorides. Fluorides can occur as particulates or as gaseous fluorides; the particulates are captured on a filter, and the gaseous fluorides are captured in a chemical reaction with water.

Samples for either Method 13A or Method 13B are obtained by the procedures outlined in Method 5 for particulates. As the gas stream passes through the sampling apparatus, the gaseous fluorides are removed by a chemical reaction with water, the particulate fluorides

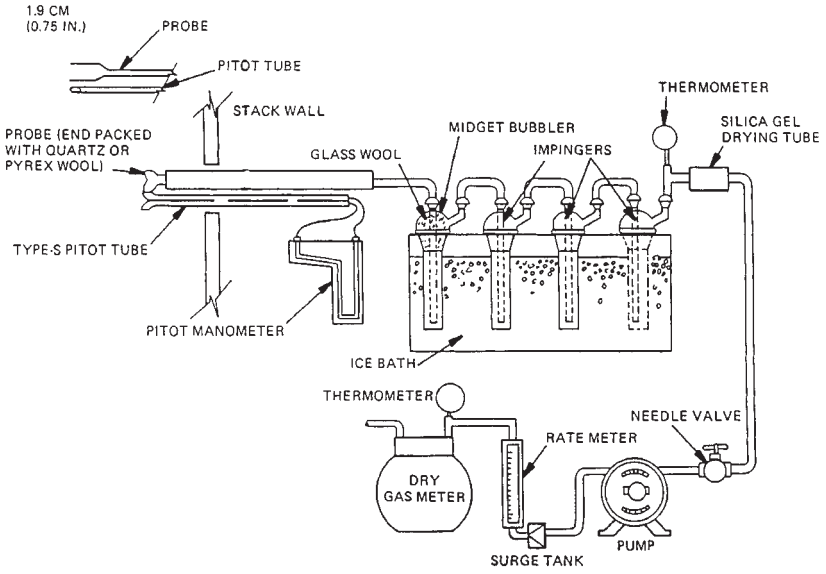


FIG. 25-33 EPA Method 6 sulfur dioxide sample train.

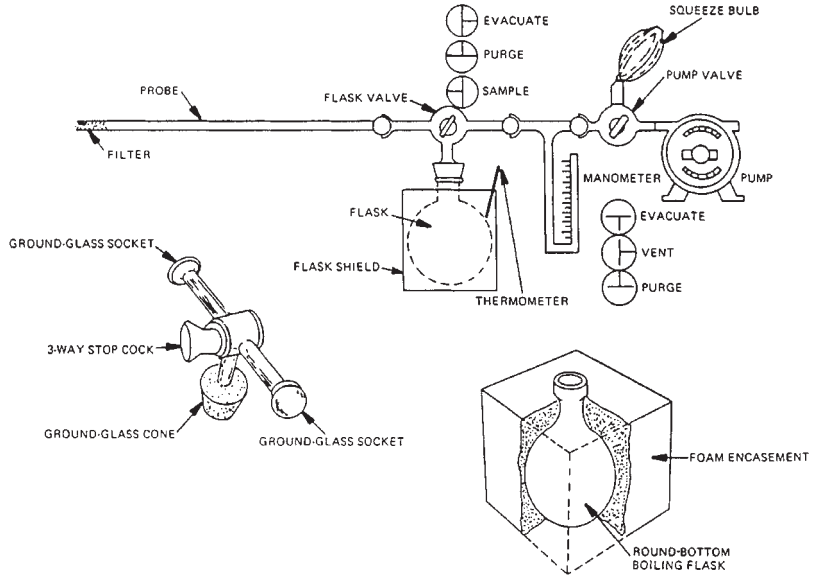


FIG. 25-34 EPA Method 7 nitrogen oxide sample train.

are captured on a filter, and the sample volume is measured. The sample is recovered and sent to the laboratory for analysis. Procedures of Methods 13A and 13B are complex and should be performed by an experienced chemist. Method 13A is a colorimetric method, and Method 13B utilizes a specific ion electrode.

A one-hour sampling period is generally required for both methods. Sampling periods are specified by the applicable standard; e.g., standards applicable to triple-superphosphate plants require sampling of one hour or more. The standard may also specify a minimum sample volume that will dictate the minimum length of the sampling period.

The determination range of Method 13A is 0 to 1.4 μg of fluoride per milliliter; the range of Method 13B is 0.02 to 2000 μg of fluoride per milliliter. Figure 25-37 is a schematic of an assembled fluoride sampling apparatus used in Methods 13A and 13B.

Total Gaseous Organics Concentration The U.S. EPA has published two reference-source testing methods for determination of total gaseous organics: EPA Method 25 for the determination of total gaseous nonmethane organics (TGNMO) and EPA Method 25A as the instrumental analyzer method for determination of total gaseous organics.

Method 25 applies to the measurement of volatile organic compounds (VOC) as nonmethane organics (TGNMO), reported as carbon. Organic particulate matter will interfere with the analysis, and, therefore, in some cases, an in-stack particulate filter will be required. The method requires an emission sample to be withdrawn at a con-

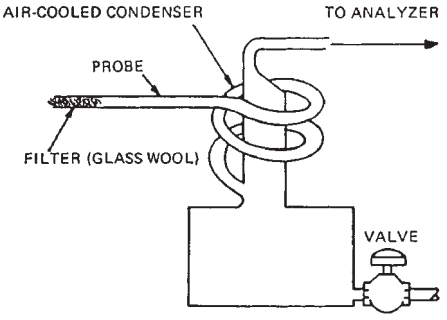


FIG. 25-35 Continuous sample train for CO.

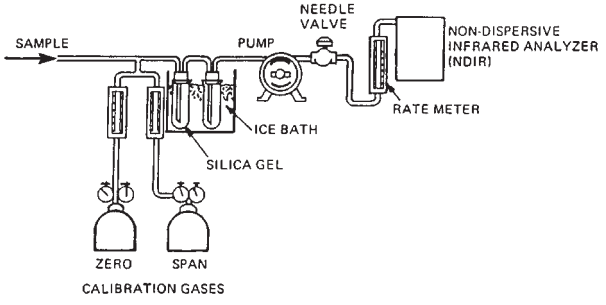


FIG. 25-36 Sampling apparatus for CO.

stant rate through a chilled-condensate trap by means of an evacuated-sample tank.

TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate-trap and sample-tank fractions. After sampling has been completed, the organic contents of the condensate trap are oxidized to carbon dioxide, which is quantitatively collected in an evacuate vessel; then a portion of the CO_2 is reduced to methane and measured by a flame ionization detector (FID). The organic content of the sample fraction collected in the sampling tank is measured by a chromatographic column to achieve separation of the nonmethane organics from carbon monoxide (CO), CO_2, and CH_4; the nonmethane organics (NMO) are oxidized to CO_2, reduced to CH_4, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

The sampling system consists of a condensate trap, flow-control system, and sample tank (Fig. 25-38). The analytical system consists of two major subsystems: an oxidation system for the recovery and conditioning of the condensate-trap contents and an NMO analyzer. The NMO analyzer is a gas chromatograph with backflush capability for NMO analysis and is equipped with an oxidation catalyst, a reduction catalyst, and an FID. The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel.

EPA Method 25A is the instrumental analyzer method for determination of total gaseous organic concentration using a flame ionization analyzer. The method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer

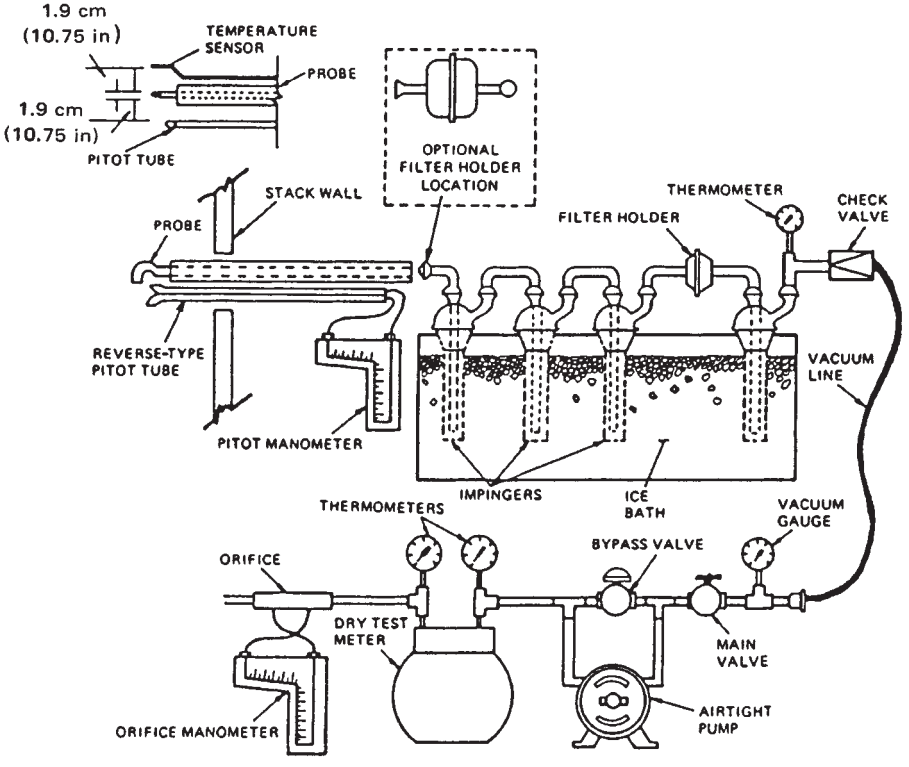


FIG. 25-37 Sampling apparatus for fluoride.

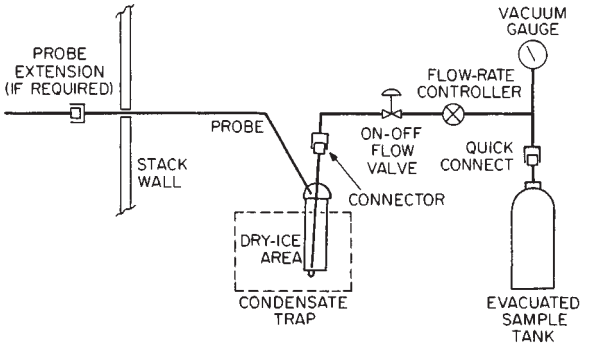


FIG. 25-38 EPA Method 25 sampling system.

(FIA). Figure 25-39 presents a schematic of the sampling system. Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

The upper limit of a gas concentration measurement range is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, a span value equivalent to 1.5 to 2.5 times the expected concentration is used. For convenience, the span value should correspond to 100 percent of the recorder scale.

Hydrogen Chloride (HCl) EPA Method 26 is the reference method used to measure hydrogen chloride emissions from stationary sources. The method is applicable for determining emissions of hydrogen halides (HX) such as hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen fluoride (HF), and halogens (X_2) like chlorine (Cl_2) and bromine (Br_2), from stationary sources. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions that collect the gaseous hydrogen halides and halogens, respectively. The filter collects other particulate matter, including halide salts. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution, where they are hydrolyzed to form a proton (H+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that two halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling, are potential interferents. Interferents for the halide measurements are the halogen gases, which disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution. The simultaneous presence of HBr and Cl_2 may cause a positive bias in the HCl result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split. High concentrations of nitrogen oxides (NO_x) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^- levels.

The collected Cl^- samples can be stored for up to 4 weeks. The ana-

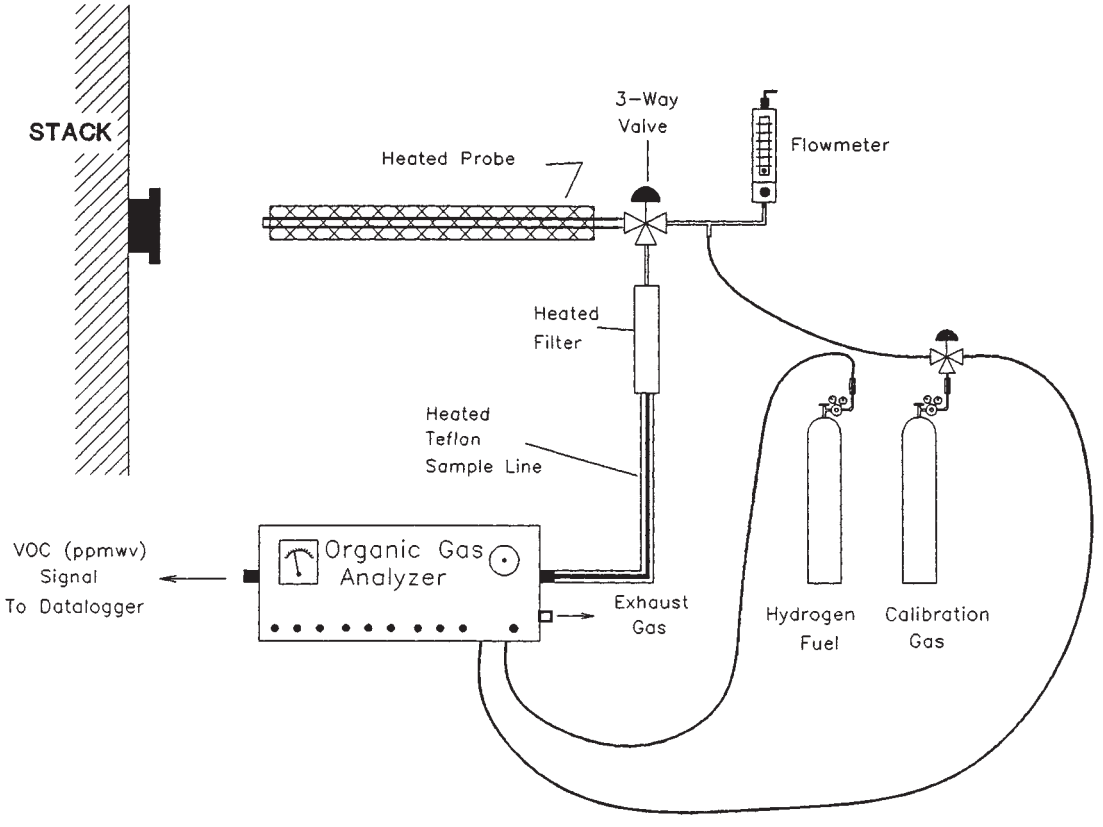


FIG. 25-39 Measurement system schematic for continuous emissions sampling for total gaseous organics.

lytical detection limit for Cl^- is 0.1 μg/ml. Detection limits for the other analyses should be similar.

The previous discussion of test methods has reviewed selected reference methods contained in Title 40 the Code of Federal Regulations, Part 60 (40 CFR 60), Appendix A. The following subsections review test methods contained in other regulations and publications. These additional test methods are employed at a greater frequency as emissions of hazardous air pollutants have become increasingly regulated. The regulatory citation for each method is provided in the narrative for each test procedure reviewed. In addition, Table 26-22 provides a reference listing of selected test methods.

Multiple Metals Testing The sampling method commonly used to measure emissions of metals from stationary sources is contained in 40 CFR 266, Appendix IX. The procedure is titled "Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes." It is also currently published as Draft EPA Method 29 for inclusion in 40 CFR 60.

This method is used for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) stack emissions from stationary sources. This method may also be used for the determination of particulate emissions following the procedures and precautions described. However, modifications to the sample recovery and analysis procedures described in the method for the purpose of determining particulate emissions may potentially impact the front-half mercury determination.

The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide in each of two impingers, and acidic potassium permanganate solution in each of two impingers (see Fig. 25-40). Sampling train components are recovered and digested in separate front- and back-half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve organics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr® Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, the HCl rinse solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold-vapor atomic absorption spectroscopy (CVAAS). The nitric acid and hydrogen peroxide solution and the probe rinse and digested filter solutions of the train catches are analyzed for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP.

Volatile Organics Sampling EPA Method 0030 as contained in *Test Methods for Evaluating Solid Waste*, 3d ed., Report No. SW-846, is used to measure emissions of volatile organic compounds with boiling points less than 100° C. Method 0030 is designed to determine destruction and removal efficiency (DRE) of volatile principal organic hazardous constituents (POHCs) from stack gas effluents of hazardous waste incinerators. The lower boiling point POHCs (less than

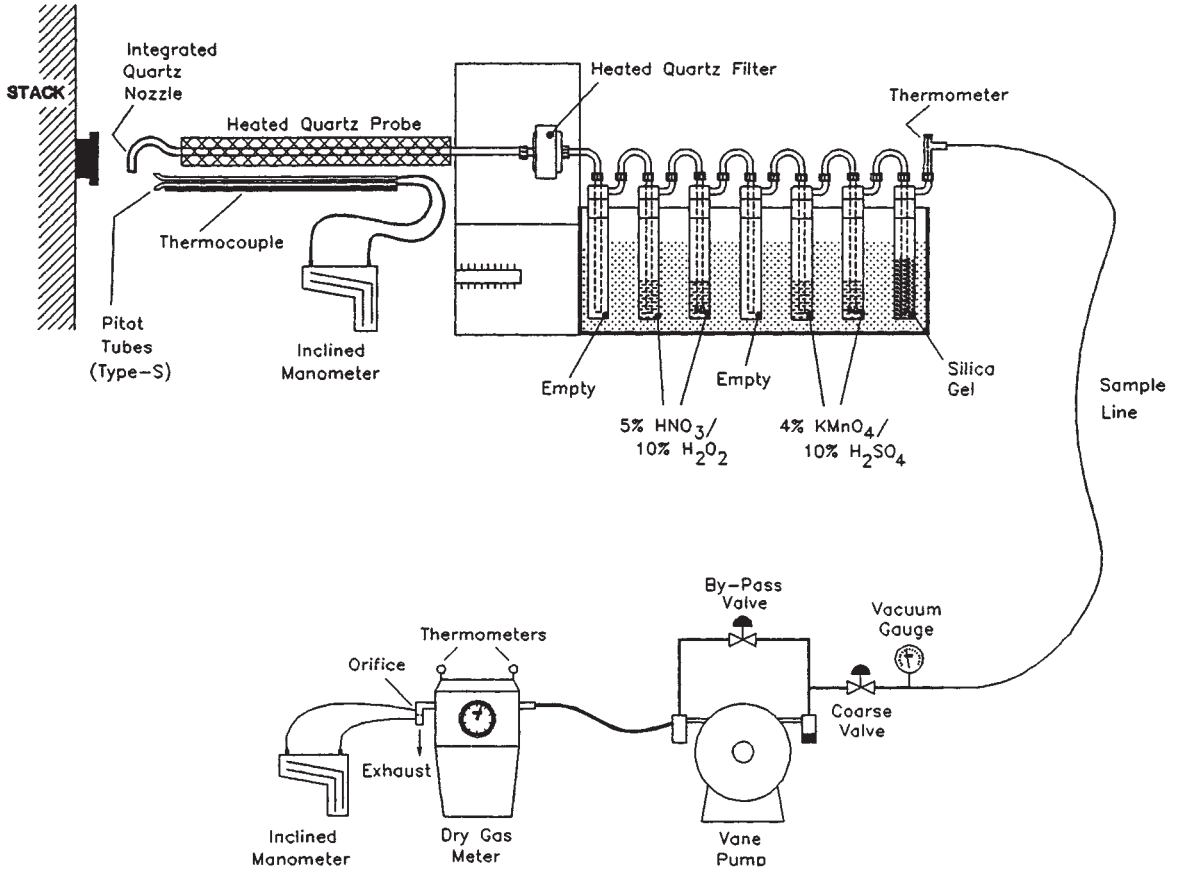


FIG. 25-40 Multiple-metals sampling train.

30° C) may break through the sorbent under the conditions of the sample collection procedure.

The procedure involves withdrawing a 20-L sample of effluent gas from the source at a flow rate of 1 L/min, using a glass-lined probe and a volatile organic sampling train (VOST). Figure 25-41 provides a schematic of the VOST set-up. The gas sample is cooled to 20° C by passage through a water-cooled condenser and volatile POHCs are collected on a pair of sorbent resin traps. Liquid condensate is collected in an impinger placed between the two resin traps. The first resin trap (front trap) contains approximately 1.6 g Tenax® resin and the second trap (back trap) contains approximately 1 g each of Tenax® and petroleum-based charcoal, 3:1 by volume. The first trap retains most of the higher boiling analytes. Lower boiling analytes and the portion of the higher boiling analytes that break through the first cartridge are retained on the second trap. Analytes that collect in the condensate trap are purged into the second trap and condenser units. The VOST sorbent cartridges are thermally desorpted and analyzed by gas chromatography with mass spectroscopy (GC/MS).

Semivolatile Organics Sampling EPA Method 0010 as contained in *Test Methods for Evaluating Solid Waste*, 3d ed., Report No. SW-846, is used to measure emissions of semivolatile principal organic constituents. Method 0010 is designed to determine destruction and removal efficiency (DRE) of POHCs from incineration systems. The method involves a modification of the EPA Method 5 sampling train and may be used to determine particulate emission rates from stationary sources. The method is applied to semivolatile compounds, including polychlorinated biphenyls (PCBs), chlorinated dibenzodioxins and dibenzofurans, polycyclic organic matter, and other semivolatile organic compounds.

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and collected in a multicomponent sampling train. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin (typically XAD-2® or polyurethane foam for PCBs). The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species (compounds with a boiling point above 100° C). Figure 25-42 presents an illustration of the Method 0010 sampling train. Comprehensive chemical analyses, using a variety of applicable analytical methodologies, are conducted to determine the identity and concentration of the organic materials.

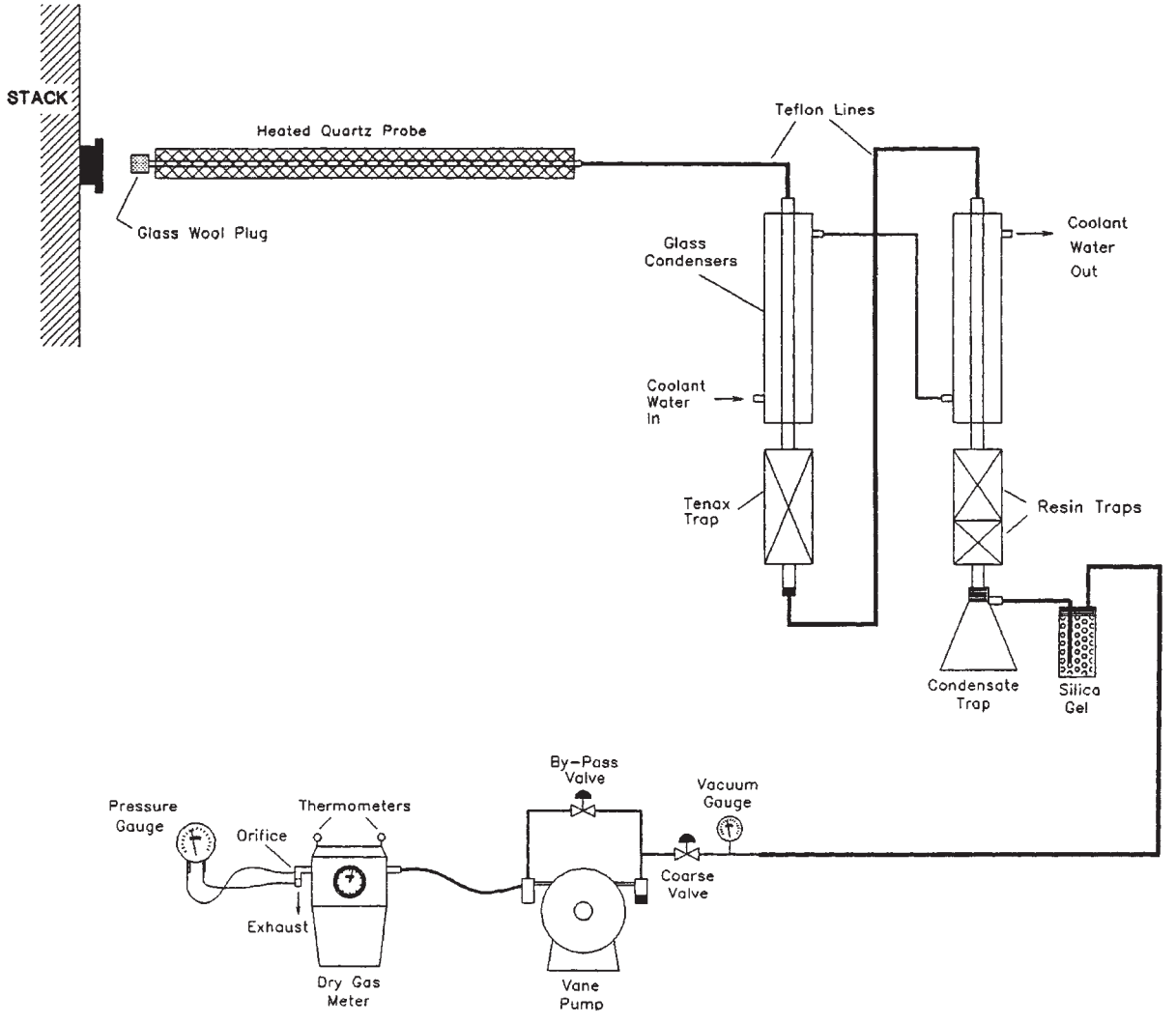


FIG. 25-41 Volatile organic sampling train (Method 0030).

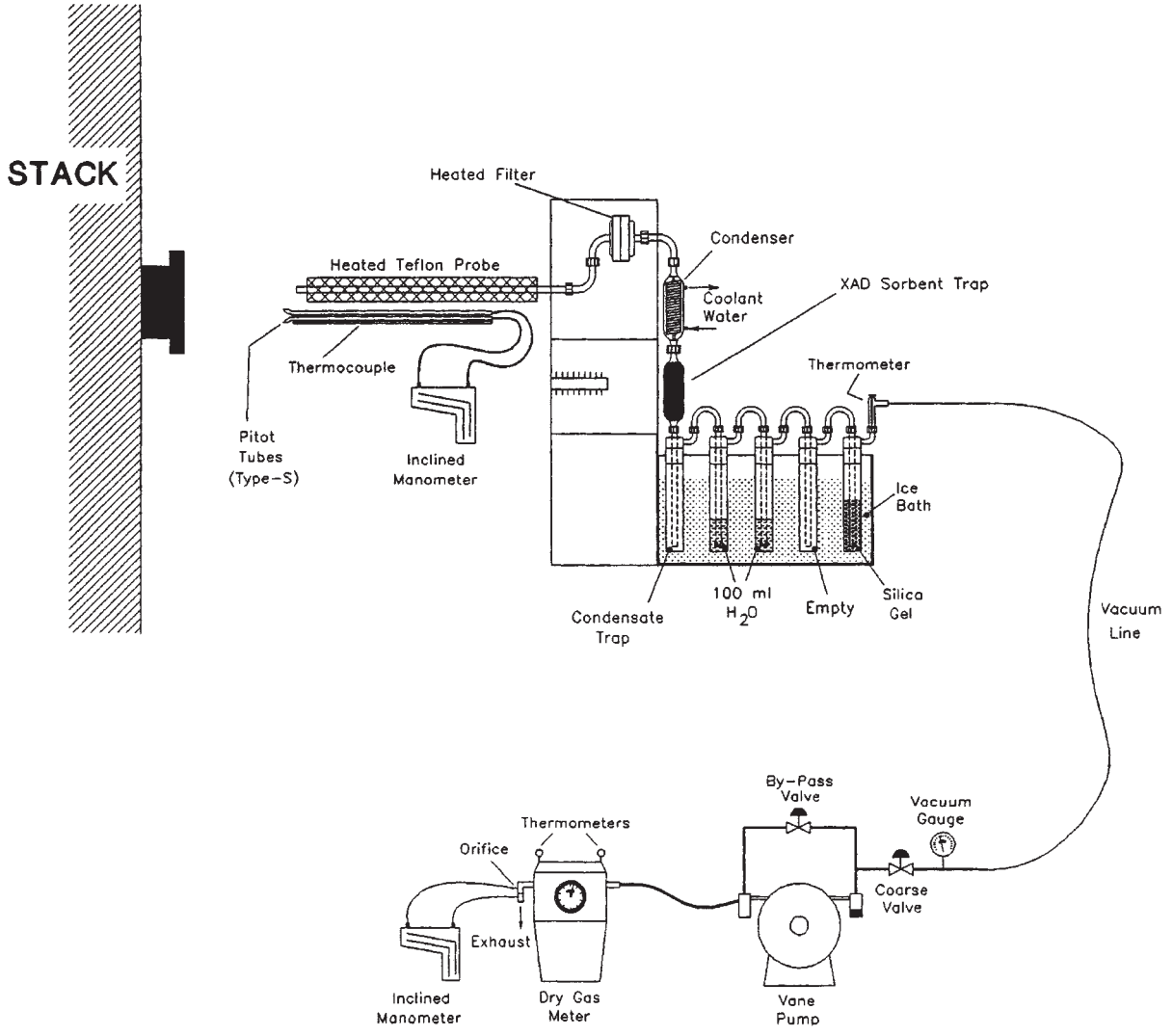


FIG. 25-42 Method 0010: sampling train for semivolatile organics.

INDUSTRIAL WASTEWATER MANAGEMENT

FURTHER READING: Eckenfelder, W. W., *Industrial Water Pollution Control,* 2d ed., McGraw-Hill, 1989. Metcalf & Eddy, Inc., *Wastewater Engineering, Treatment, Disposal and Reuse,* 3d ed., McGraw-Hill, 1990. Nemerow, N. L. and A. Dasgupta, Industrial and Hazardous Waste Treatment, Van Nostrand Reinhold, New York, 1991.

INTRODUCTION

All industrial operations produce some wastewaters which must be returned to the environment. Wastewaters can be classified as (1) domestic wastewaters, (2) process wastewaters, and (3) cooling wastewaters. Domestic wastewaters are produced by plant workers, shower facilities, and cafeterias. Process wastewaters result from spills, leaks, and product washing. Cooling wastewaters are the result of various cooling processes and can be once-pass systems or multiple-recycle cooling systems. Once-pass cooling systems employ large volumes of cooling waters that are used once and returned to the environment. Multiple-recycle cooling systems have various types of cooling towers to return excess heat to the environment and require periodic blowdown to prevent excess buildup of salts.

Domestic wastewaters are generally handled by the normal sanitary-sewerage system to prevent the spread of pathogenic microorganisms which might cause disease. Normally, process wastewaters do not pose the potential for pathogenic microorganisms, but they do pose potential damage to the environment through either direct or indirect chemical reactions. Some process wastes are readily biodegraded and create an immediate oxygen demand. Other process wastes are toxic and represent a direct health hazard to biological life in the environment. Cooling wastewaters are the least dangerous, but they can contain process wastewaters as a result of leaks in the cooling systems. Recycle cooling systems tend to concentrate both inorganic and organic contaminants to a point at which damage can be created.

Recently, concern for subtle aspects of environmental damage has started to take precedence over damage referred to above. It has been realized that the presence of substances in water at concentrations far below those that will produce overt toxicity or excessive reduction of dissolved oxygen levels can have a major impact by altering the predomination of organisms in the aquatic ecosystem. This is beginning to have an effect on water-quality standards and, consequently, allowable discharges. Unfortunately, the extent of knowledge is not sufficient upon which to base definitive standards for these subtle effects. Over the next decade, it is anticipated that accumulation of knowledge will make it possible to delineate defensible standards. Another recent concern is that of contaminated storm water from industrial sites. Federal guidelines to control this wastewater are presently being developed. Most concern is for product spills on plant property but outside the production facility and from rain contact with spoil piles.

UNITED STATES LEGISLATION, REGULATIONS, AND GOVERNMENTAL AGENCIES

Federal Legislation Public Law 92-500 promulgated in 1972 created the primary framework for management of water pollution in the United States. This act has been amended many times since 1972. Major amendments occurred in 1977 (Public Laws 95-217 and 95-576), 1981 (Public Laws 97-117 and 97-164), and 1987 (Public Law 100-4). This law and its various amendments are referred to as the Clean Water Act. The Clean Water Act addresses a large number of issues of water pollution management. A general review of these issues has been presented in an earlier chapter in this handbook. Primary with respect to control of industrial wastewater is the National Pollutant Discharge Elimination System (NPDES), originally established by PL 92-500. Any municipality or industry that discharges wastewater to the navigable waters of the United States must obtain a discharge permit under the regulations set forth by the NPDES. Under this system, there are three classes of pollutants (conventional pollutants, priority pollutants, and nonconventional/nonpriority pollutants). Conventional pollutants are substances such as biochemical oxygen demand (BOD), suspended solids (SS), pH, oil and grease, and coliforms. Priority pollutants are a list of 129 substances originally set forth in a consent decree between the Environmental Protection Agency and several environmental organizations. This list was incorporated into the 1977 amendments. Most of the substances on this list are organics, but it does include most of the heavy metals. These substances are generally considered to be toxic. However, the toxicity is not absolute; it depends on the concentration. In addition, many of the organics on the list are under appropriate conditions biodegradable. In reality, substances for inclusion on the priority pollutant list were chosen on the basis of a risk assessment rather than only a hazard assessment. The third class of pollutants could include any pollutant not in the first two categories. Examples of substances that are presently regulated in the third category are nitrogen, phosphorous, sodium, and chlorine residual. The overall goals of the Clean Water Act are to restore and maintain water quality in the navigable waters of the United States. The initial standard was to ensure that these waters would be clean enough for recreation (swimmable) and ecologically secure (fishable). Initially this was to be achieved by curtailment of the discharge of pollutants. Eventually the regulatory system was essentially to phase out discharge of any pollutant into water. Obviously, if no discharge of pollutants occurs, the waters will be maintained in close to a pristine condition. However, the early reduction of pollutant discharge to zero was realized as impractical. Thus, at present, the NPDES has prescribed the limits on discharges as a function of the type of pollutant, the type of industry discharging, and the desired water quality. The specific requirements for each individual discharger are established in the NPDES permit issued to the discharger. These permits are reviewed every five years and are subject to change at the time of review.

A major tactic that was adopted in the Clean Water Act was to establish uniform technology standards, by class of pollutant and specific industry type, which applied nationwide to all dischargers. Thus, a kraft mill in Oregon would have to meet essentially the same discharge standards as a kraft mill in New York. In establishing these standards, the EPA took into account the state of the art of waste treatment in each particular industry as well as cost and ecological effectiveness. These discharge standards have been published in the *Federal Register* for more than thirty industrial categories and several hundred subcategories (the Commerce Department Industrial Classification System was used to establish these categories) in the *Federal Register*. These have been promulgated over an extensive period of time. The reader is advised to consult the index to this document to ascertain regulations that apply to a particular industry. Table 25-32 presents the major industrial categories.

As indicated above, not only are the discharge standards organized on an industry-by-industry basis, but they are different depending upon which of the three classes of pollutants is being regulated. The standards for conventional pollutants are referred to as best conventional technology (BCT). The standards for priority pollutants are referred to as best available technology (BAT), as are those for nonconventional, nonpriority pollutants. These standards envision that the technology will not be limited to treatment but may include revision in the industrial processing and/or reuse of effluents (pollution prevention). They are usually presented as mass of pollutant discharged per unit of product produced.

In some situations it is anticipated that application of BCT and BAT may not be sufficient to ensure that water-quality standards are achieved in a stream segment. Studies have indicated that approximately 10 percent of the stream segments in the United States will have their water-quality standards violated, even if all the dischargers to that stream segment meet BCT and BAT regulations. These segments are referred to as water quality limited segments. The NPDES permit for those who discharge into water quality limited segments must provide for pollutant removal in excess of that required by BCT and BAT so that water-quality standards (which are jointly established by each state and EPA) are achieved. The stream segments in which water-quality standards will be met by application of BCT and BAT are referred to as "effluent quality limited segments."

For industrial discharges that enter municipal sewers and thus eventually municipal treatment plants, NPDES regulations are nominally the same as for industries that discharge directly to navigable

TABLE 25-32 Industry Categories

1. Adhesives and sealants
2. Aluminum forming
3. Asbestos manufacturing
4. Auto and other laundries
5. Battery manufacturing
6. Coal mining
7. Coil coating
8. Copper forming
9. Electric and electronic components
10. Electroplating
11. Explosives manufacturing
12. Ferroalloys
13. Foundries
14. Gum and wood chemicals
15. Inorganic chemicals manufacturing
16. Iron and steel manufacturing
17. Leather tanning and finishing
18. Mechanical products manufacturing
19. Nonferrous metals manufacturing
20. Ore mining
21. Organic chemicals manufacturing
22. Pesticides
23. Petroleum refining
24. Pharmaceutical preparations
25. Photographic equipment and supplies
26. Plastic and synthetic materials manufacturing
27. Plastic processing
28. Porcelain enamelling
29. Printing and publishing
30. Pulp and paperboard mills
31. Soap and detergent manufacturing
32. Steam electric power plants
33. Textile mills
34. Timber products processing

waters; i.e., they must meet BCT and BAT standards. These are referred to as "categorical industrial pretreatment standards." However if it can be demonstrated that the municipal treatment plant can remove a pollutant in the industrial waste, a "removal credit" can be assigned to the permit, thus lowering the requirement on the industrial discharger. The monetary charge to the industry by the municipality for this service is negotiable but must be within parameters established by EPA for industrial user charges if the municipality received a federal grant for construction of the treatment plant. A removal credit cannot be assigned if removal of the industrial pollutant results in difficulty in ultimate disposal of sludge from the municipal plant. In addition, an industry cannot discharge any substance that can result in physical damage to the municipal sewer and/or interfere with any aspect of treatment plant performance even, if the substance is not covered by BCT or BAT regulations.

Environmental Protection Agency President Nixon created the EPA in 1970 to coordinate all environmental pollution-control activities at the federal level. The EPA was placed directly under the Office of the President so that it could be more responsive to the political process. In the succeeding decade, the EPA produced a series of federal regulations increasing federal control over all wastewater-pollution-control activities. In January 1981, President Reagan reversed the trend of greater federal regulation and began to decrease the role of the federal EPA. However, during the 1980s, an equilibrium was achieved between those who wish less regulation and those who wish more. In general, industry and the EPA reached agreement on the optimum level of regulation.

State Water-Pollution-Control Offices Every state has its own water-pollution-control office. Some states have reorganized along the lines of the federal EPA with state EPA offices, while others have kept their water-pollution-control offices within state health departments. Prior to 1965, each state controlled its own water-pollution-control programs. Conflicts between state and uneven enforcement of state regulations resulted in the federal government's assuming the leadership role. Unfortunately, conflicts between states shifted to being conflicts between the states and the federal EPA. By 1980, the state water-pollution-control offices were primarily concerned with handling most of the detailed permit and paperwork for the EPA and in furnishing technical assistance to industries at the local level. In general, most of the details of regulation are carried out by state water-pollution-control agencies with oversight by EPA.

WASTEWATER CHARACTERISTICS

Wastewater characteristics vary widely from industry to industry. Obviously, the specific characteristics will affect the treatment techniques chosen for use in meeting discharge requirements. Some general characteristics that should be considered in planning are given in Table 25-33. Because of the large number of pollutant substances, wastewater characteristics are not usually considered on a substance-by-substance basis. Rather, substances of similar pollution effects are grouped together into classes of pollutants or characteristics as indicated below.

TABLE 25-33 Wastewater Characteristics

Property	Characteristic	Example	Size or concentration
Solubility	Soluble	Sugar	>100 gm/L
	Insoluble	PCB	<1 mg/L
Stability, biological	Degradable	Sugar	
	Refractory	DDT, metals	
Solids	Dissolved	NaCl	$<10^{-9}$ m
	Colloidal	Carbon	$>10^{-6}$–$<10^{-9}$ m
	Suspended	Bacterium	$>10^{-6}$ m
Organic	Carbon	Alcohol	
Inorganic	Inorganic	Cu^{2+}	
pH	Acidic	HNO_3	
	Neutral	Salt (NaCl)	1–12
	Basic	NaOH	
Temperature	High–low	Cooling	>5°
		Heat exchange	>30°
Toxicity	Biological effect	Heavy metals	Varies
		Priority compounds	
Nutrients	N	NH_3	Varies
	P	PO_4^{3-}	

Priority Pollutants Recently, greatest concern has been for this class of substances for the reasons given previously. These materials are treated on an individual-substance basis for regulatory control. Thus, each industry could receive a discharge permit that lists an acceptable level for each priority pollutant. Table 25-34 presents a list of these substances; most are organic, but some inorganics are included. All are considered toxic, but, as indicated previously, there is wide variation in their toxicity. Most of the organics are biologically degradable despite their toxicity (Refs. 30 and 31). USEPA has collected data on the occurrence of these substances in various industrial wastes and their treatability. A recent trend has been to avoid their use in industrial processing.

Organics The organic composition of industrial wastes varies widely, primarily due to the different raw materials used by each specific industry. These organics include proteins, carbohydrates, fats and oils, petrochemicals, solvents, pharmaceutical, small and large molecules, solids and liquids. Another complication is that a typical industry produces many diverse wastestreams. Good practice is to conduct a material balance throughout an entire production facility. This survey should include a flow diagram, location and sizes of piping, tanks and flow volumes, as well as an analysis of each stream. Results of an industrial waste survey for an industry are given in Table 25-35. Noteworthy is the range in waste sources, including organic soap, toilet articles, ABS (alkyl benzene sulfonate), and the relatively clean but hot condenser water that makes up half the plant flow, while the strongest wastes—spent caustic and fly ash—have the lowest flows. See Tables 25-35 and 25-36 for information on the average characteristics of wastes from specific industries.

An important measure of the waste organic strength is the 5-day biochemical oxygen demand (BOD_5). As this test measures the demand for oxygen in the water environment caused by organics released by industry and municipalities, it has been the primary parameter in determining the strength and effects of a pollutant. This test determines the oxygen demand of a waste exposed to biological organisms (controlled seed) for an incubation period of five days. Usually this demand is caused by degradation of organics according to the following simplified equation, but reduced inorganics in some industries may also cause demand (i.e., Fe^{2+}, S^{2-}, and SO_3^{2-}).

$$\text{Organic waste} + O_2\ (\text{D.O.}) \xrightarrow[\text{microbes}]{\text{seed}} CO_2 + H_2O$$

This wet lab test measures the decrease in dissolved oxygen (D.O.) concentration in 5 days, which is then related to the sample strength. If the test is extended over 20 days, the BOD_{20} (ultimate BOD) is obtained and corresponds more closely to the Chemical Oxygen Demand (COD) test. The COD test uses strong chemical oxidizing agents with catalysts and heat to oxidize the wastewater and obtain a value that is almost always larger than the 5- and 20-day BOD values. Some organic compounds (like pyridene, a ring structure containing nitrogen) resists chemical oxidation giving a low COD. A major advantage of the COD test is the completion time of less than 3 hours, versus 5 days for the BOD_5 test. Unfortunately, state and federal regulations generally require BOD_5 values, but approximate correlations can be made to allow computation of BOD from COD. A more rapid measure of the organic content of a waste is the instrumental test for total organic carbon (TOC), which takes a few minutes and may be correlated to both COD and BOD for specific wastes. Unfortunately, BOD_5 results are subject to wide statistical variations and require close scrutiny and experience. For municipal wastewaters, BOD_5 is about 67 percent of the ultimate BOD and 40–45 percent of the COD, indicating a large amount of nonbiodegradable COD and the continuing need to run BOD as well as COD and TOC. An example of BOD, COD, and TOC relationships for chemical industry wastewater is given in Table 25-36. The concentrations of the wastewaters vary by two orders of magnitude, and the BOD/COD, COD/TOC, and BOD/TOC ratios vary less than twofold. The table indicates that correlation/codification is possible, but care and continual scrutiny must be exercised.

TABLE 25-34 List of Priority Chemicals*

Compound name
1. Acenaphthene†
2. Acrolein†
3. Acrylonitrile†
4. Benzene†
5. Benzidine†
6. Carbon tetrachloride† (tetrachloromethane)
Chlorinated benzenes (other than dichlorobenzenes)
7. Chlorobenzene
8. 1,2,4-Trichlorobenzene
9. Hexachlorobenzene
Chlorinated ethanes† (including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)
10. 1,2-Dichloroethane
11. 1,1,1-Trichloroethane
12. Hexachloroethane
13. 1,1-Dichloroethane
14. 1,1,2-Trichloroethane
15. 1,1,2,2-Tetrachloroethane
16. Chloroethane (ethyl chloride)
Chloroalkyl ethers† (chloromethyl, chloroethyl, and mixed ethers)
17. Bis(chloromethyl) ether
18. Bis(2-chloroethyl) ether
19. 2-Chloroethyl vinyl ether (mixed)
Chlorinated napthalene†
20. 2-Chloronapthalene
Chlorinated phenols† (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
21. 2,4,6-Trichlorophenol
22. *para*-Chloro-*meta*-cresol
23. Chloroform (trichloromethane)†
24. 2-Chlorophenol†
Dichlorobenzenes†
25. 1,2-Dichlorobenzene
26. 1,3-Dichlorobenzene
27. 1,4-Dichlorobenzene
Dichlorobenzidine†
28. 3,3′-Dichlorobenzidine
Dichloroethylenes† (1,1-dichloroethylene and 1,2-dichloroethylene)
29. 1,1-Dichloroethylene
30. 1,2-*trans*-Dichloroethylene
31. 2,4-Dichlorophenol†
Dichloropropane and dichloropropene†
32. 1,2-Dichloropropane
33. 1,2-Dichloropropylene (1,2-dichloropropene)
34. 2,4-Dimethylphenol†
Dinitrotoluene†
35. 2,4-Dinitrotoluene
36. 2,6-Dinitrotoluene
37. 1,2-Diphenylhydrazine†
38. Ethylbenzene†
39. Fluoranthene†
Haloethers† (other than those listed elsewhere)
40. 4-Chlorophenyl phenyl ether
41. 4-Bromophenyl phenyl ether
42. Bis(2-chloroisopropyl) ether
43. Bis(2-chloroethoxy) methane
Halomethanes† (other than those listed elsewhere)
44. Methylene chloride (dichloromethane)
45. Methyl chloride (chloromethane)
46. Methyl bromide (bromomethane)
47. Bromoform (tribromomethane)
48. Dichlorobromomethane
49. Trichlorofluoromethane
50. Dichlorodifluoromethane
51. Chlorodibromomethane
52. Hexachlorobutadiene†
53. Hexachlorocyclopentadiene†
54. Isophorone†
55. Naphthalene†
56. Nitrobenzene†
Nitrophenols† (including 2,4-dinitrophenol and dinitrocresol)
57. 2-Nitrophenol
58. 4-Nitrophenol
59. 2,4-Dinitrophenol†
60. 4,6-Dinitro-*o*-cresol
Nitrosamines†
61. *N*-Nitrosodimethylamine
62. *N*-Nitrosodiphenylamine
63. *N*-Nitrosodi-*n*-propylamine
64. Pentachlorophenol†
65. Phenol†
Phthalate esters†
66. Bis(2-ethylhexyl) phthalate
67. Butyl benzyl phthalate
68. Di-*n*-butyl phthalate
69. Di-*n*-octyl phthalate
70. Diethyl phthalate
71. Dimethyl phthalate
Polynuclear aromatic hydrocarbons (PAH)†
72. Benzo(a)anthracene (1,2-benzanthracene)
73. Benzo(a)pyrene (3,4-benzopyrene)
74. 3,4-Benzofluoranthene
75. Benzo(k)fluoranthene (11,12-benzofluoranthene)
76. Chrysene
77. Acenaphthylene
78. Anthracene
79. Benzo(ghl)perylene (1,12-benzoperylene)
80. Fluorene
81. Phenanthrene
82. Dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)
83. Indeno (1,2,3-cd) pyrene (2,3-*o*-phenylenepyrene)
84. Pyrene
85. Tetrachloroethylene†
86. Toluene†
87. Trichloroethylene†
88. Vinyl chloride† (chloroethylene)
Pesticides and metabolites
89. Aldrin†
90. Dieldrin†
91. Chlordane† (technical mixture and metabolites)
DDT and metabolites†
92. 4-4′-DDT
93. 4,4′-DDE (*p,p*′-DDX)
94. 4,4′-DDD (*p,p*′-TDE)
Endosulfan and metabolites†
95. α-Endosulfan-alpha
96. β-Endosulfan-beta
97. Endosulfan sulfate
Endrin and metabolites†
98. Endrin
99. Endrin aldehyde
Heptachlor and metabolites†
100. Heptachlor
101. Heptachlor epoxide
Hexachlorocyclohexane (all isomers)†
102. α-BHC-alpha
103. β-BHC-beta
104. γ-BHC (lindane)-gamma
105. δ-BHC-delta
Polychlorinated biphenyls (PCB)†
106. PCB-1242 (Arochlor 1242)
107. PCB-1254 (Arochlor 1254)
108. PCB-1221 (Arochlor 1221)
109. PCB-1232 (Arochlor 1232)
110. PCB-1248 (Arochlor 1248)
111. PCB-1260 (Arochlor 1260)
112. PCB-1016 (Arochlor 1016)
113. Toxaphene†
114. antimony (total)
115. arsenic (total)
116. asbestos (fibrous)
117. beryllium (total)
118. cadmium (total)
119. chromium (total)
120. copper (total)
121. cyanide (total)
122. lead (total)
123. mercury (total)
124. nickel (total)
125. selenium (total)
126. silver (total)
127. thallium (total)
128. zinc (total)
129. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

*Adapted from Eckenfelder, W. W. Jr., *Industrial Water Pollution Control,* 2d ed., McGraw-Hill, New York, 1989.
†Specific compounds and chemical classes as listed in the consent degree.

Another technique for organics measurement that overcomes the long period required for the BOD test is the use of continuous respirometry. Here the waste (full-strength rather than diluted as in the standard BOD test) is contacted with biomass in an apparatus that continuously measures the dissolved oxygen consumption. This test determines the ultimate BOD in a few hours if a high level of biomass is used. The test can also yield information on toxicity, the need to develop an acclimated biomass, and required rates of oxygen supply.

In general, low-molecular-weight water-soluble organics are biodegraded readily. As organic complexity increases, solubility and biodegradability decrease. Soluble organics are metabolized more easily than insoluble organics. Complex carbohydrates, proteins, and fats and oils must be hydrolyzed to simple sugars, aminos, and other organic acids prior to metabolism. Petrochemicals, pulp and paper,

TABLE 25-35 Industrial Waste Components of a Soap, Detergents, and Toilet Articles Plant

Waste source	Sampling station	COD, mg/l	BOD, mg/l	SS, mg/l	ABS, mg/l	Flow, gal/min
Liquid soap	*D*	1,100	565	195	28	300
Toilet articles	*E*	2,680	1,540	810	69	50
Soap production	*R*	29	16	39	2	30
ABS production	*S*	1,440	380	309	600	110
Powerhouse	*P*	66	10	50	0	550
Condenser	*C*	59	21	24	0	1100
Spent caustic	*B*	30,000	10,000	563	5	2
Tank bottoms	*A*	120,000	150,000	426	20	1.5
Fly ash	*F*			6750		10
Main sewer		450	260	120	37	2150

NOTE: gal/min = 3.78×10^{-3} m^3/min.
SOURCE: Eckenfelder, W. W., *Industrial Water Pollution Control,* 2d ed., McGraw-Hill, New York, 1989.

TABLE 25-36 BOD, COD, and TOC Relationships

Type of waste	BOD_5, mg/L	COD, mg/L	TOC, mg/L	BOD_5/COD	COD/TOC	BOD_5/TOC
Chemical	700	1,400	450	0.50	3.12	1.55
Chemical	850	1,900	580	0.45	3.28	1.47
Chemical	8,000	17,500	5,800	0.46	3.02	1.38
Chemical	9,700	15,000	5,500	0.65	2.72	1.76
Chemical	24,000	41,300	9,500	0.58	4.35	2.53
Chemical	60,700	78,000	26,000	0.78	3.00	2.34
Chemical	62,000	143,000	48,140	0.43	2.96	1.28

Adapted from Eckenfelder, W.W. and D.L. Ford, *Water Pollution Control,* Pemberton Press, Austin and New York, 1970.

slaughterhouse, brewery, and numerous other industrial wastes containing complex organics have been satisfactorily treated biologically, but proper testing and evaluation is necessary.

Inorganics The inorganics in most industrial wastes are the direct result of inorganic compounds in the carriage water. Soft-water sources will have lower inorganics than hard-water or saltwater sources. However, some industrial wastewaters can contain significant quantities of inorganics which result from chemical additions during plant operation. Many food processing wastewaters are high in sodium. While domestic wastewaters have a balance in organics and inorganics, many process wastewaters from industry are deficient in specific inorganic compounds. Biodegradation of organic compounds requires adequate nitrogen, phosphorus, iron, and trace salts. Ammonium salts or nitrate salts can provide the nitrogen, while phosphates supply the phosphorus. Either ferrous or ferric salts or even normal steel corrosion can supply the needed iron. Other trace elements needed for biodegradation are potassium, calcium, magnesium, cobalt, molybdenum, chloride, and sulfur. Carriage water or demineralizer wastewaters or corrosion products can supply the needed trace elements for good metabolism. Occasionally, it is necessary to add specific trace elements or nutrient elements.

pH and Alkalinity Wastewaters should have pH values between 6 and 9 for minimum impact on the environment. Wastewaters with pH values less than 6 will tend to be corrosive as a result of the excess hydrogen ions. On the other hand, raising the pH above 9 will cause some of the metal ions to precipitate as carbonates or as hydroxides at higher pH levels. Alkalinity is important in keeping pH values at the right levels. Bicarbonate alkalinity is the primary buffer in wastewaters. It is important to have adequate alkalinity to neutralize the acid waste components as well as those formed by partial metabolism of organics. Many neutral organics such as carbohydrates, aldehydes, ketones, and alcohols are biodegraded through organic acids which must be neutralized by the available alkalinity. If alkalinity is inadequate, sodium carbonate is a better form to add than lime. Lime tends to be hard to control accurately and results in high pH levels and precipitation of the calcium which forms part of the alkalinity. In a few instances, sodium bicarbonate may be the best source of alkalinity.

Temperature Most industrial wastes tend to be on the warm side. For the most part, temperature is not a critical issue below 37° C if wastewaters are to receive biological treatment. It is possible to operate thermophilic biological wastewater-treatment systems up to 65° C with acclimated microbes. Low-temperature operations in northern climates can result in very low winter temperatures and slow reaction rates for both biological treatment systems and chemical treatment systems. Increased viscosity of wastewaters at low temperatures makes solid separation more difficult. Efforts are generally made to keep operating temperatures between 10 and 30° C if possible.

Dissolved Oxygen Oxygen is a critical environmental resource in receiving streams and lakes. Aquatic life requires reasonable dissolved-oxygen (DO) levels. EPA has set minimum stream DO levels at 5 mg/L during summer operations, when the rate of biological metabolism is a maximum. It is important that wastewaters have maximum DO levels when they are discharged and have a minimum of oxygen-demanding components so that DO remains above 5 mg/L. DO is a poorly soluble gas in water, having a solubility around 9.1 mg/L at 20° C and 101.3-kPa (1-atm) air pressure. As the temperature increases and the pressure decreases with higher elevations above sea level, the solubility of oxygen decreases. Thus, DO is a minimum when BOD rates are a maximum. Lowering the temperature yields higher levels of DO saturation, but the biological metabolism rate decreases. Warm-wastewater discharges tend to aggravate the DO situation in receiving waters.

Solids Total solids is the residue remaining from a wastewater dried at 103–105° C. It includes the fractions shown in Fig. 25-43. The first separation is the portion that passes through a 2-μm filter (dissolved) and those solids captured on the filter (suspended). Combustion at 500° C further separates the solids into volatile and ash (fixed) solids. Although ash and volatile solids do not distinguish inorganic from organic solids exactly, due to loss of inorganics on combustion, the volatile fraction is often used as an approximate representation of the organics present. Another type of solids, settleable solids, refers to solids that settle in an Imhoff cone in one hour. Industrial wastes vary substantially in these types of solids and require individual wastewater treatment process analysis. An example of possible variation is given in Table 25-37.

Nutrients and Eutrophication Nitrogen and phosphorus cause significant problems in the environment and require special attention in industrial wastes. Nitrogen, phosphorus, or both may cause aquatic biological productivity to increase, resulting in low dissolved oxygen and eutrophication of lakes, rivers, estuaries, and marine waters. Table 25-38 gives the primary nutrient forms causing problems, while the following equation shows the biological oxidation or oxygen-consuming potential of the most common nitrogen forms.

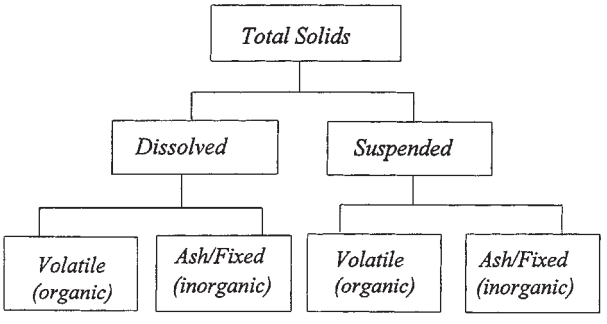


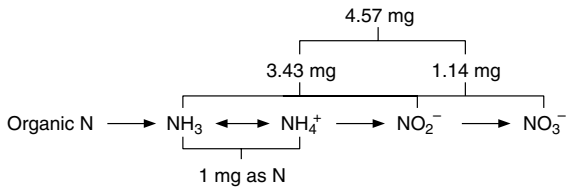
FIG. 25-43 Solids identification. Abbreviations: TS, total solids; SS, suspended solid; D, dissolved; V, volatile.

TABLE 25-37 Solids Variation in Industrial Wastewater

Type of solids	Plating	Pulp and paper
Total	High	High
Dissolved	High	High
Suspended	Low	High
Organic	Low	High
Inorganic	High	High

TABLE 25-38 Nutrient Forms

Parameter	Example
Organic N	protein
Ammonia	NH_3
Ammonium	NH_4^+
Nitrite	NO_2^-
Nitrate	NO_3^-
Organic P	malathion
Ortho-P	PO_4^{3-}
Poly-P	$(PO_4^{3-})_x$



When organics containing reduced nitrogen are degraded, they usually produce ammonium, which is in equilibrium with ammonia. As the pK for $NH_3 \leftrightarrow NH_4^+$ is 9.3, the ammonium ion is the primary form present in virtually all biological treatment systems, as they operate at pH < 8.5 and usually in the pH range of 6.5–7.5. In aerobic reactions, ammonium is oxidized by nitrifying bacteria (nitrosomonas) to nitrite and each mg of NH_4^+—N oxidized will require 3.43 mg D.O. Further oxidation of nitrite by nitrobacter yields nitrate and uses an additional 1.14 mg of D.O. for a total D.O. consumption of 4.57 mg. Thus, organic and ammonium nitrogen can exert significant biochemical oxygen demand in the water environment. This nitrogen demand is referred to as nitrogenous or NBOD, whereas organic BOD is CBOD (carbonaceous). In treatment of wastewaters with organics and ammonium, the total oxygen demand (TOD) may have to be satisfied in accordance with the approximate formula:

$$TOD \cong 1.5\ BOD_5 + 4.5\ (TKN)$$

where TKN (total Kjeldahl nitrogen) = Organic N + NH_4^+—N.

Phosphorus is not oxidized or reduced biologically, but ortho-P may be formed from organic and poly-P. Ortho-P may be removed by chemical precipitation or biologically with sludges and will be covered in a later section.

While many industrial wastes are so low in nitrogen and phosphorus that these must be added if biologically based treatment is to be used, others contain very high levels of these nutrients. For example, paint-production wastes are high in nitrogen, and detergent production wastes are high in phosphorus. Treatment for removal of these nutrients is required in areas where eutrophication is a problem.

Oil and Grease These substances are found in many industrial wastes (i.e., meat packing, petrochemical, and soap production). They tend to float on the water surface, blocking oxygen transfer, interfering with recreation, and producing an aesthetically poor appearance in the water. Measurement is by a solvent extraction procedure. Many somewhat different substances will register as oil and grease in this test. Often oil and grease interfere with other treatment operations, so they must be removed as part of the initial stages of treatment.

WASTEWATER TREATMENT

As indicated above, industrial wastewater contains a vast array of pollutants in soluble, colloidal, and particulate forms, both inorganic and organic. In addition, the required effluent standards are also diverse, varying with the industrial and pollutant class. Consequently, there can be no standard design for industrial water-pollution control. Rather, each site requires a customized design to achieve optimum performance. However, each of the many proven processes for industrial waste treatment is able to remove more than one type of pollutant and is in general applicable to more than one industry. In the sections that follow, waste-treatment processes are discussed more from the broad-based generalized perspective than with narrow specificity. Generally, a combination of several processes is utilized to achieve the degree of treatment required at the least cost.

Much of the experience and data from wastewater treatment has been gained from municipal treatment plants. Industrial liquid wastes are similar to wastewater but differ in significant ways. Thus, typical design parameters and standards developed for municipal wastewater operations must not be blindly utilized for industrial wastewater. It is best to run laboratory and small pilot tests with the specific industrial wastewater as part of the design process. It is most important to understand the temporal variations in industrial wastewater strength, flow, and waste components and their effect on the performance of various treatment processes. Industry personnel in an effort to reduce cost often neglect laboratory and pilot studies and depend on waste characteristics from similar plants. This strategy often results in failure, delay, and increased costs. Careful studies on the actual waste at a plant site cannot be overemphasized.

PRETREATMENT

Many industrial-wastewater streams should be pretreated prior to discharge to municipal sewerage systems or even to a central industrial sewerage system. Pretreatment of individual streams should be considered whenever these streams might have an adverse effect on the total treatment system.

Equalization Equalization is one of the most important pretreatment devices. The batch discharge of concentrated wastes is best suited for equalization. It may be important to equalize wastewater flows, wastewater concentrations, or both. Periodic wastewater discharges tend to overload treatment units. Flow equalization tends to level out the hydraulic loads on treatment units. It may or may not level out concentration variations, depending upon the extent of mixing within the equalization basin. Mechanical mixing may be adequate if the wastes are purely chemical in their reactivity. Biodegradable wastes normally require aeration mixing so that the microbes are kept aerobic and nuisance odors are prevented. Diffused aeration systems offer better mixing under variable load conditions than mechanical surface aeration equipment. Mixing and oxygen transfer are both important with biodegradable wastewaters. Operation on regular cycles determines the size of the equalization basin. There is no advantage in making the equalization basin any larger than necessary to level out wastewater variations. Industrial operation on a 5-day, 40-h week will normally make a 2-day equalization basin as large as needed for continuous operation of the wastewater-treatment system under uniform conditions.

Neutralization Acidic or basic wastewaters must be neutralized prior to discharge. If an industry produces both acidic and basic wastes, these wastes may be mixed together at the proper rates to obtain neutral pH levels. Equalization basins can be used as neutralization basins. When separate chemical neutralization is required, sodium hydroxide is the easiest base material to handle in a liquid form and can be used at various concentrations for in-line neutralization with a minimum of equipment. Yet, lime remains the most widely used base for acid neutralization. Limestone is used when reaction rates are slow and considerable time is available for reaction. Sulfuric acid is the primary acid used to neutralize high-pH wastewaters unless calcium sulfate might be precipitated as a result of the neutralization reaction. Hydrochloric acid can be used for neutralization of basic wastes if sulfuric acid is not acceptable. For very weak basic wastewaters carbon dioxide can be adequate for neutralization.

Grease and Oil Removal Grease and oils tend to form insoluble layers with water as a result of their hydrophobic characteristics. These hydrophobic materials can be easily separated from the water phase by gravity and simple skimming, provided they are not too well mixed with the water prior to separation. If the oils and greases form emulsions with water as a result of turbulent mixing, the emulsions are difficult to break. Separation of oil and grease should be carried out near the point of their mixing with water. In a few instances, air bubbles can be added to the oil and grease mixtures to separate the hydrophobic materials from the water phase by flotation. Chemicals have also been added to help break the emulsions. American Petro-

leum Institute (API) separators have been used extensively by the petroleum industry to remove oils from wastewaters. The food industries use grease traps to collect the grease prior to its discharge. Unfortunately, grease traps are designed for regular cleaning of the trapped grease. Too often they are allowed to fill up and discharge the excess grease into the sewer or are flushed with hot water and steam to fluidize the grease for easy discharge to the sewer. A grease trap should be designed for a specific volume of grease to be collected over specific time periods. Care should be taken to design the trap so that the grease can easily be removed and properly handled. Neglected or poorly designed grease traps are worse than no grease traps at all.

Toxic Substances Recent federal legislation has made it illegal for industries to discharge toxic materials in wastewaters. Each industry is responsible for determining if any of its wastewater components are toxic to the environment and to remove them prior to the wastewater discharge. The EPA has identified a number of priority pollutants which must be removed and kept under proper control from their origin to their point of ultimate disposal. Major emphasis has recently been placed on heavy metals and on complex organics that have been implicated in possible cancer production. Pretreatment is essential to reduce heavy metals below toxic levels and to prevent discharge of any toxic organics. Fortunately, toxic organics can ultimately be destroyed by various chemical oxidation systems. Incineration appears to be the most economical method for destroying toxic organics. To make incineration economical, the organics must be kept separated from the dilute wastewaters and treated in their concentrated form. If the heavy metals cannot be reused, they must be concentrated and placed into insoluble materials which will not leach the heavy metals. Toxic substances currently pose the greatest challenge to industries since very little attention has been paid to these materials in the past.

PRIMARY TREATMENT

Wastewater treatment is directed toward removal of pollutants with the least effort. Suspended solids are removed by either physical or chemical separation techniques and handled as concentrated solids.

Screens Fine screens such as hydroscreens are used to remove moderate-size particles that are not easily compressed under fluid flow. Fine screens are normally used when the quantities of screened particles are large enough to justify the additional units. Mechanically cleaned fine screens have been used for separating large particles. A few industries have used large bar screens to catch large solids that could clog or damage pumps or equipment following the screens.

Grit Chambers Industries with sand or hard, inert particles in their wastewaters have found aerated grit chambers useful for the rapid separation of these inert particles. Aerated grit chambers are relatively small, with total volume based on 3-min retention at maximum flow. Diffused air is normally used to create the mixing pattern shown in Fig. 25-44, with the heavy, inert particles removed by centrifugal action and friction against the tank walls. The air flow rate is adjusted for the specific particles to be removed. Floatable solids are removed in the aerated grit chamber. It is important to provide for regular removal of floatable solids from the surface of the grit chamber; otherwise, nuisance conditions will be created. The settled grit is normally removed with a continuous screw and buried in a landfill.

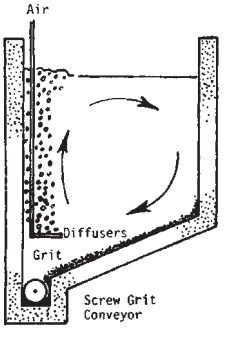


FIG. 25-44 Schematic diagram of an aerated grit chamber.

Gravity Sedimentation Slowly settling particles are removed with gravity sedimentation tanks. For the most part, these tanks are designed on the basis of retention time, surface overflow rate, and minimum depth. A sedimentation tank can be rectangular or circular. The important factor affecting its removal efficiency is the hydraulic flow pattern through the tank. The energy contained in the incoming-wastewater flow must be dissipated before the solids can settle. The wastewater flow must be distributed properly through the sedimentation volume for maximum settling efficiency. After the solids have settled, the settled effluent should be collected without creating serious hydraulic currents that could adversely affect the sedimentation process. Effluent weirs are placed at the end of rectangular sedimentation tanks and around the periphery of circular sedimentation tanks to ensure uniform flow out of the tanks. Once the solids have settled, they must be removed from the sedimentation-tank floor by scraping and hydraulic flow. Conventional sedimentation tanks have sludge hoppers to collect the concentrated sludge and to prevent removal of excess volumes of water with the settled solids. Cross-sectional diagrams of conventional sedimentation tanks are shown in Figs. 25-45 and 25-46.

Design criteria for gravity sedimentation tanks normally provide for 2-h retention based on average flow, with longer retention periods used for light solids or inert solids that do not change during their retention in the tank. Care should be taken that sedimentation time is not too long; otherwise, the solids will compact too densely and affect solids collection and removal. Organic solids generally will not compact to more than 5 to 10 percent. Inorganic solids will compact up to 20 or 30 percent. Centrifugal sludge pumps can handle solids up to 5 or 6 percent, while positive-displacement sludge pumps can handle solids up to 10 percent. With solids above 10 percent the sludge tends to lose fluid properties and must be handled as a semi-solid rather than a fluid. Circular sedimentation tanks have steel truss boxes with angled sludge scrapers on the lower side. As the sludge scrapers rotate, the solids are pushed toward the sludge hopper for removal on a continuous or semicontinuous basis. The rectangular sedimentation tanks employ chain-and-flight sludge collectors or rail-mounted sludge collectors. When floating solids can occur in primary sedimentation tanks, surface skimmers are mounted on the sludge scrapers so that the surface solids are removed at regular intervals.

The surface overflow rate (SOR) for primary sedimentation is normally held close to 40.74 $m^3/(m^2 \cdot day)$ [1000 $gal/(ft^2 \cdot day)$] for average flow rates, depending upon the solids characteristics. Lowering the SOR below 40.74 $m^3/(m^2 \cdot day)$ does not produce improved effluent

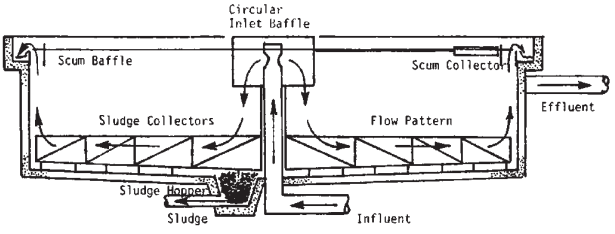


FIG. 25-45 Schematic diagram of a circular sedimentation tank.

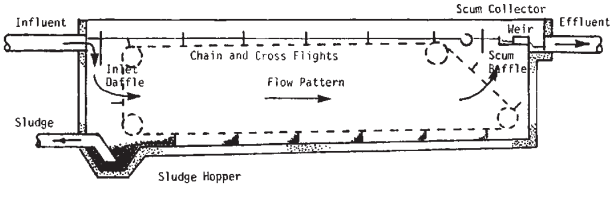


FIG. 25-46 Schematic diagram of a rectangular sedimentation tank.

quality in proportion to the reduction in SOR. Generally, the minimum depth of sedimentation tanks is 3.0 m (10 ft), with circular sedimentation tanks having a minimum diameter of 6.0 m (20 ft) and rectangular sedimentation tanks having length-to-width ratios of 5:1. Chain-and-flight limitations generally keep the width of rectangular sedimentation tanks to increments of 6.0 m (20 ft) or less. While hydraulic overflow rates have been limited on the effluent weirs, operating experience has indicated that the recommended limit of 186 $m^3/(m \cdot day)$ [15,000 gal/(ft·day)] is lower than necessary for good operation. A circular sedimentation tank with a single-edge weir provides adequate weir length and is easier to adjust than one with a double-sided weir. More problems appear to be created from improper adjustment of the effluent weirs than from improper length.

Chemical Precipitation Lightweight suspended solids and colloidal solids can be removed by chemical precipitation and gravity sedimentation. In effect, the chemical precipitate is used to agglomerate the tiny particles into large particles that settle rapidly in normal sedimentation tanks. Aluminum sulfate, ferric chloride, ferrous sulfate, lime, and polyelectrolytes have been used as coagulants. The choice of coagulant depends upon the chemical characteristics of the particles being removed, the pH of the wastewaters, and the cost and availability of the precipitants. While the precipitation reaction results in removal of the suspended solids, it increases the amount of sludge to be handled. The chemical sludge must be considered along with the characteristics of the original suspended solids in evaluating sludge-processing systems.

Normally, chemical precipitation requires a rapid mixing system and a flocculation system ahead of the sedimentation tank. With a rectangular sedimentation tank, the rapid-mixer and flocculation units are added ahead of the tank. With a circular sedimentation tank the rapid-mixer and flocculation units are built into the tank. Schematic diagrams of chemical treatment systems are shown in Figs. 25-47 and 25-48. Rapid mixers are designed to provide 30-s retention at average flow with sufficient turbulence to mix the chemicals with the incoming wastewaters. The flocculation units are designed for slow mixing at 20-min retention. These units are designed to cause the particles to collide and increase in size without excessive shearing. Care must be taken to move the flocculated mixture from the flocculation unit to the sedimentation unit without disrupting the large floc particles.

The parameter used to design rapid mix and flocculation systems is the root mean square velocity gradient G, which is defined by equation

$$G = \left(\frac{P}{VU}\right)^{1/2} \left(\frac{1}{\text{sec}}\right)$$

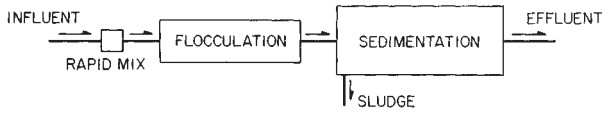


FIG. 25-47 Schematic diagram of a chemical precipitation system for rectangular sedimentation tanks.

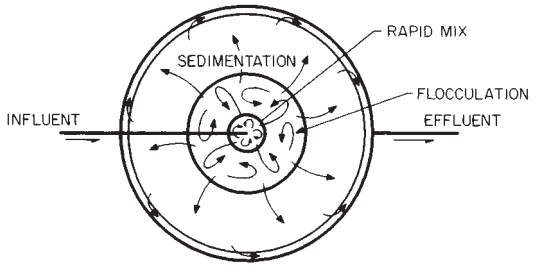


FIG. 25-48 Schematic diagram of a chemical precipitation system for circular sedimentation tanks.

where: P = Power input to the water (ft·lb/sec)
V = Mixer or flocculator volume $(ft)^3$
U = Absolute viscosity of water (lb·sec/ft^2)

Optimum mixing usually requires a G value of greater than 1000 inverse seconds. Optimum flocculation occurs when G is in the range 10–100 inverse seconds.

Chemical precipitation can remove 95 percent of the suspended solids, up to 50 percent of the soluble organics and the bulk of the heavy metals in a wastewater. Removal of soluble organics is a function of the coagulant chemical, with iron salts yielding best results and lime the poorest. Metal removal is primarily a function of pH and the ionic state of the metal. Guidance is available from solubility product data.

SECONDARY TREATMENT

Secondary treatment utilizes processes in which microorganisms, primarily bacteria, stabilize waste components. The mixture of microorganisms is usually referred to as biomass. A portion of the waste is oxidized, releasing energy, the remainder is utilized as building blocks of protoplasm. The energy released by biomass metabolism is utilized to produce the new units of protoplasm. Thus, the incentive for the biomass to stabilize waste is that it provides the energy and basic chemical components required for reproduction. The process of biological waste conversion is illustrated by Eq. (25-15).

$$\text{Waste (electron donor)} + \text{Biomass} + \text{Electron acceptor} \xrightarrow[\text{environmental conditions}]{\text{Proper}} \text{More biomass} + \text{End products: Oxidized electron donor, Reduced electron acceptor} \qquad (25\text{-}15)$$

As this equation indicates, the waste generally serves as an electron donor, necessitating that an electron acceptor be supplied. A variety of substances can be utilized as electron acceptors, including molecular oxygen, carbon dioxide, oxidized forms of nitrogen, sulfur, and organic substances. The characteristics of the end products of the reaction are determined by the electron acceptor. Table 25-39 is a list of typical end products as a function of the electron acceptor. In general, the end products of this reaction are at a much lower energy level than the waste components, thus resulting in the release of energy referred to above. Although this process is usually utilized for the stabilization of organic substances, it can also be utilized for oxidation of inorganics. For example, biomass-mediated oxidation of iron, nitrogen, and sulfur is known to occur in nature and in anthropogenic processes.

Equation (25-15) describes the biomass-mediated reaction and indicates that proper environmental conditions are required for the reaction to take place. These conditions are required by the biomass, not the electron donor or acceptor. The environmental conditions include pH, temperature, nutrients, ionic balance, and so on. In general, biomass can function over a wide pH range generally from 5 to 9. However, some microbes require a much narrower pH range; i.e., effective methane fermentation requires a pH in the range of 6.5–7.5. It is just as important to maintain a relatively constant pH in the process as it is to stay within the range given above. Microorganisms can function effectively at the extremes of their pH range provided they are given the opportunity to acclimate to these conditions. Continual changes in pH are detrimental, even if the organisms are on the average near the middle of their effective pH range. A similar situa-

TABLE 25-39 Electron Acceptors and End Products for Biological Reactions

Electron acceptors	End product
Molecular oxygen	Water, CO_2, oxidized nitrogen
Oxidized nitrogen	N_2, N_2O, NO, CO_2, H_2O
Oxidized sulfur	H_2S, S, CO_2, H_2O
CO_2, acetic acid, formic acid	CH_4, CO_2, H_2
Complex organics	H_2, simple organics, CO_2, H_2O

tion prevails for temperature. Most organisms can function well over a broad range of temperature but do not adjust well to frequent fluctuations of even a few degrees. There are three major temperature ranges in which microorganisms function. The psychrophilic range (5° C to 20° C), the mesophilic range (20° C to 45° C), and the thermophilic range (45° C to 70° C). In general the microbes that function in one of these temperature ranges cannot function efficiently in the other ranges. As it is generally uneconomical to adjust the temperature of a waste, most processes are operated in the mesophilic range. If the normal temperature of the waste is above or below the mesophilic range, the process will be operated in the psychrophilic or thermophilic range as appropriate. However, occasionally the temperature of the waste is altered to improve performance. For example, some anaerobic treatment processes are operated under thermophilic conditions, even though the waste must be heated to achieve this temperature range. This is carried out in order to speed up the degradation of complex organics and/or to achieve kill of mesophilic pathogens. It should be noted that any time the biological operation of a process moves away from its optimum or most effective range, be it pH, temperature, nutrients, or what have you, the rate of biological processing is reduced.

All microorganisms require varying amounts of a large number of nutrients. These are required because they are necessary components of bacterial protoplasm. The nutrients can be divided into three groups: macro, minor, and micro. The macronutrients are those that comprise most of the biomass. These are given by the commonly accepted formula for biomass ($C_{60}H_{87}O_{23}N_{12}P$). The carbon, hydrogen, and oxygen are normally supplied by the waste and water, but the nitrogen and phosphorous must often be added to industrial wastes to ensure that a sufficient amount is present. A good rule is that the mass of nitrogen should be at least 5 percent of the BOD, and the mass of phosphorous should be at least 20 percent of the mass of nitrogen. One of the major operational expenses is the purchase of nitrogen and phosphorous for addition to biologically based treatment processes. The quantities of nitrogen and phosphorous referred to above as required are actually in excess of the minimum amounts needed. The actual amount required depends upon the quantity of excess biomass wasted from the system and the amount of N and P available in the waste. This will be expanded upon later in this section. The minor nutrients include the typical inorganic components of water. These are given in Table 25-40. The range of concentrations required in the wastewater for the minor nutrients is 1–100 mg/L. The micronutrients include the substances that we normally refer to as trace metals and vitamins. It is interesting to note that the trace metals include virtually all of the toxic heavy metals. This reinforces the statement made above that toxicity is a function of concentration and not an absolute parameter. Whether or not the substances referred to as vitamins will be required depends upon the type of microorganisms required to stabilize the waste materials. Many microorganisms have the ability to make their own vitamins from the waste components; thus, a supplement is not needed. However, occasionally the addition of an external source of vitamins is essential to the success of a biologically based waste-treatment system. In general, the trace nutrients must be present in a waste at a level of a few micrograms per liter.

One aspect of the basic equation describing biological treatment of waste that has not been referred to previously is that biomass appears on both sides of the equation. As was indicated above, the only reason that microorganisms function in waste-treatment systems is because it enables them to reproduce. Thus, the quantity of biomass in a waste-treatment system is higher after the treatment process than before it.

TABLE 25-40 Minor and Micro Nutrients Required for Biologically Mediated Reactors

Minor 1–100 mg/L
Sodium, potassium, calcium, magnesium, iron, chloride, sulfate
Micro 1–100 μg/L
Copper, cobalt, nickel, manganese, boron, vanadium, zinc, lead, molybdenum, various organic vitamins, various amino acids

This is favorable in that there is a continual production of the organisms required to stabilize the waste. Thus, one of the major reactants is, in effect, available free of charge. However, there is an unfavorable side in that unless some organisms are wasted from the system, an excess level will build up, and the process could choke on organisms. The wasted organisms are referred to as sludge. A major cost component of all biologically based processes is the need to provide for the ultimate disposal of this sludge.

Biologically based treatment processes probably account for the majority of the treatment systems used for industrial waste management because of their low cost and because most substances are amenable to biological breakdown. However, some substances are difficult to degrade biologically. Unfortunately, it is not possible at present to predict a priori the biodegradability of a specific organic compound; rather, we must depend upon experience and testing. The collective experience of the field has been put into compendia by EPA in a variety of documents. However, these data are primarily qualitative. There have been some attempts to develop a system of prediction of biodegradability based on a number of compound parameters such as solubility, presence or absence of certain functional groups, compound polarity, and so on. Unfortunately, none of these systems has advanced to the point where reliable quantitative predictions are possible. Another complication is that some organics that are easily biodegradable at low concentration exert a toxic effect at high concentration. Thus, literature data can be confusing. Phenol is a typical compound that shows ease of biodegradation when the concentration is below 500 mg/L but poor biodegradation at higher concentrations. Another factor affecting both biodegradation and toxicity is whether or not a substance is in solution. In general, if a substance is not in solution, it is not available to affect the biomass. Thus, the presence of a waste in substances that can precipitate, complex, or absorb other waste components can have a significant effect on reports of biodegradability and/or toxicity. A quantitative estimate of toxicity can be obtained in terms of the change in kinetic parameters of a system. These kinetic parameters are discussed below.

Design of Biological Treatment Systems In the past, the design of biologically based waste-treatment systems has been derived from rules of thumb. During the past two decades, however, a more fundamental system has been developed and is presently widely used to design such systems. This system is based upon a fundamental understanding of the kinetics and stoichiometry of biological reactions. The system is codified in terms of equations in which four pseudo constants appear. These pseudo constants are k_m, the maximum substrate utilization rate (1/time); K_s, the half maximal velocity concentration (mg/L); Y, the yield coefficient; and b, the endogenous respiration rate (1/time). These are referred to as pseudo constants because, in the mathematical manipulation of the equations in which they appear, they are treated as constants. However, the value of each is a function of the nature of the microbes, the pH, the temperature, and the components of the waste. It is important to remember that if any of these change, the value of the pseudo constants may change as well. The kinetics of biological reactions are described by Eq. (25-16).

$$\frac{dS}{dt} = \frac{k_m S X}{K_s + S} \tag{25-16}$$

where t = time (days)
S = waste concentration (mg/L)
X = biomass concentration (mg/L)
k_m = (mg/L substrate ÷ mg/L biomass) – time

The accumulation or growth of biosolids is given by Eq. (25-17).

$$\frac{dX}{dt} = Y\frac{dS}{dt} - bX \tag{25-17}$$

where X = biomass level (mg/L).

The equations that have been developed for design using these pseudo constants are based on steady-state mass balances of the biomass and the waste components around both the reactor of the system and the device used to separate and recycle microorganisms. Thus, the equations that can be derived will be dependent upon the characteristics of the reactor and the separator. It is impossible here to

present equations for all the different types of systems. As an illustration, the equations for a common system (a complete mix – stirred tank reactor with recycle) are presented below.

$$S_e = \frac{K_s[1 + \text{BSRT}(b)]}{\text{BSRT}(YK_m - b) - 1} \quad (25\text{-}18)$$

$$X = \frac{(\text{BSRT})(Y)(S_o - S_e)}{\text{HRT}[1 + (b)\text{BSRT}]} \quad (25\text{-}19)$$

where: S_e = influent waste concentration (mg/L)
S_o = treated waste concentration (mg/L)
HRT = reactor hydraulic retention time

Note that these equations predict some unexpected results. The strength of the untreated waste (S_o) has no effect on the strength of the treated waste (S_e). Neither does the size of the reactor (HRT). Rather, a parameter referred to as the biomass solids retention time (BSRT) is the key parameter determining the system performance. This is illustrated in Fig. 25-49. As the BSRT increases, the concentration of untreated waste in the effluent decreases irrespective of the reactor size or the waste strength. However, the reactor size and waste strength have a significant effect on the level of biomass (X) that is maintained in the system at steady state. Since the development of an excess level of biomass in the system can lead to system upset, it is important to take cognizance of the waste strength and the reactor size. But treatment performance with respect to removal of the waste components is again a function only of BSRT and the value of the pseudo constants referred to above. The BSRT also has an effect on the level of biomass in the system and the quantity of excess biomass produced (Fig. 25-50). The latter will determine the quantity of waste sludge which must be dealt with as well as the N and P requirement. The N and P in the biomass removed from the system each day must be replaced. From the formula given previously for biomass, N is 12 percent and P is 2.3 percent by weight in biomass grown under ideal conditions (see Fig. 25-50). Also, note that m, the minimum BSRT, is the minimum time required for the microorganisms to double in mass. Below this minimum, washout occurs and substrate removal approaches zero.

Although identical results are not obtained for other reactor configurations, the design equations yield similar patterns. The dominant parameters in determining system performance are again the BSRT and the pseudo constants. The latter are not under the control of the design engineer as they are functions of the waste and the microorganisms that developed in the system. The BSRT is the major design parameter under the control of the design engineer. This parameter has been defined as the ratio of the biomass in the reactor to the biomass produced from the waste each day. At steady state, the level of biomass in the system is constant; thus, the biomass produced must equal the biomass wasted. The minimum BSRT that can be utilized is that which will produce the degree of treatment required. Generally,

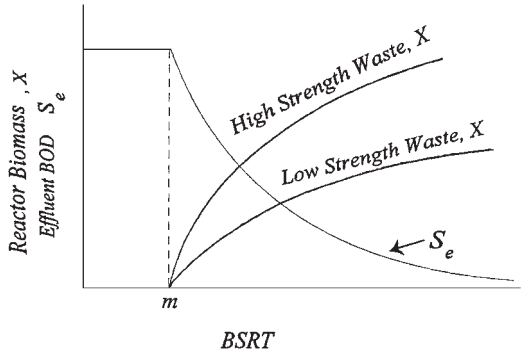


FIG. 25-49 Effect of BSRT on biological treatment process performance. m = minimum BSRT.

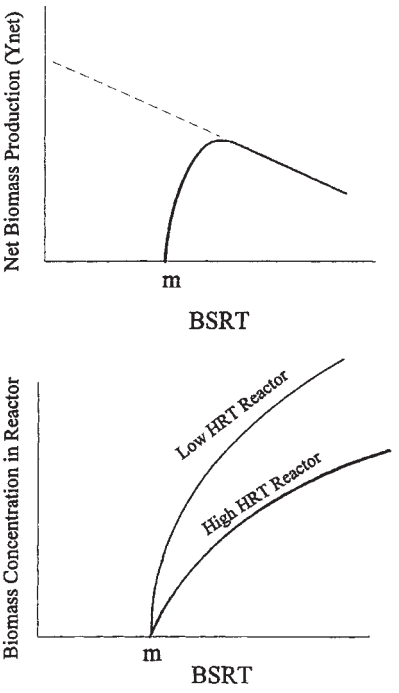


FIG. 25-50 Biomass production.

this minimum value is less than the range of BSRT used in design and operation. This provides not only a safety factor, but, in addition, it is necessary in order to foster the growth of certain favorable groups of microorganisms in the system. Generally, BSRT values in the range of 3–15 days are utilized in most systems, although BSRT values of less than 1 day for high rate systems are usually adequate to ensure greater than 95 percent destruction of waste components in all but anaerobic systems. For the latter, a minimum BSRT of 8 days is needed for 95 percent destruction. BSRT is controlled by the concentration of biomass (X) in the system and the quantity wasted each day; thus, the treatment plant operator can alter BSRT by altering the rate of biomass wasting.

Reactor Concepts A large number of reactor concepts seem to be used in biologically based treatment systems. However, this diversity is more apparent than real. In reality, there are only two major reactor types that are used. One is referred to as a suspended growth reactor, the other is referred to as a fixed film reactor. In the former, the waste and the microorganisms move through the reactor, with the microorganisms constantly suspended in the flow. After exiting the reactor, the suspension flows through a separator, which separates the organisms from the liquid. Some of the organisms are wasted as sludge, while the remainder are returned to the reactor. The supernatant is discharged either to the environment or to other treatment units (Fig. 25-51). The functioning of the separator is very important, as poor performance of the separator will result in high solids in the effluent and reduction of organisms in the recycle and eventually also in the reactor. As indicated above, the level of the BSRT used in design of suspended growth systems is set to produce a biomass of the proper level in the system; i.e., a level at which waste degradation is rapid but not so high that excess loading on the separator will occur. BSRT also influences the ability of biomass to self flocculate and thus be removed in the separator (usually a clarifier).

In the fixed-film reactor, the organisms grow on an inert surface that is maintained in the reactor. The inert surface can be granular material, proprietary plastic packing, rotating discs, wood slats, mass-transfer packing, or even a sponge-type material. The reactor can be flooded or have a mixed gas-liquid space (Fig. 25-52). The biomass level on the

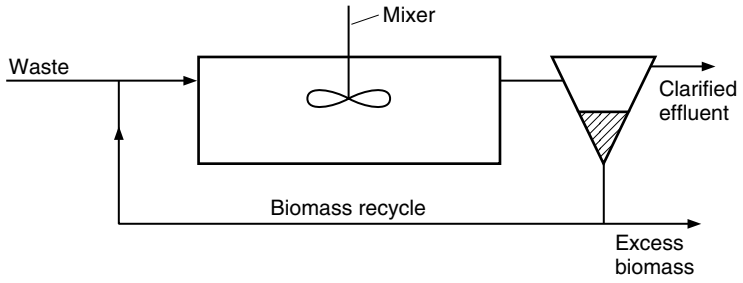


FIG. 25-51 Diagram of a suspended growth system.

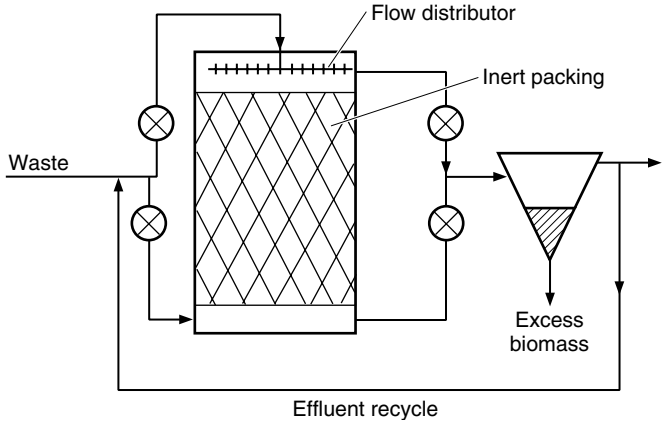


FIG. 25-52 Diagram of a fixed-film system.

packing is controlled by hydraulic scour produced as the waste liquid flows through the reactor. There is no need of a separator to ensure that the biomass level in the reactor is maintained. The specific surface area of the packing is the design parameter used to ensure an adequate level of biomass. However, a separator is usually supplied to capture biomass washed from the packing surface by the flow of the waste, thus providing a clarified effluent. As with the suspended growth system, if this biomass escapes the system, it will result in a return to the environment of organic laden material, thus negating the effectiveness of the waste treatment. As indicated above, biomass level in a fixed film reactor is maintained by a balance between the rate of growth on the packing (which is a function of the strength of the waste, the yield coefficient and the BSRT), and the rate of hydraulic flushing by the waste flow. Recycle of treated wastewater is used to control the degree of hydraulic flushing. Thus, typical design parameters for fixed film reactors include both an organic loading and a hydraulic loading. Details on the typical levels for these will be given in a later section.

The reactor concepts described above can be utilized with any of the electron acceptor systems previously discussed, although some reactor types perform better with specific electron acceptors. For example, suspended growth systems are generally superior to fixed film systems when molecular oxygen is the electron acceptor because it is easier to supply oxygen to suspended growth systems.

On the other hand, fixed film systems are superior for systems in which nitrate is the electron acceptor because the nitrogen bubbles produced in suspended growth systems tend to float sludge to the top of the clarifiers used as biomass separators. Another factor affecting reactor type and electron acceptor selection is waste strength. The higher the waste strength, the higher the level of biomass in the reactor and vice versa. When waste strength is low, fixed film reactors are favored as it is easier to maintain an adequate biomass level. When waste strength is high, it is better to use anaerobic electron acceptors than aerobic because oxygen supply is not limiting for anaerobic systems. In addition, the yield coefficient Y is much lower for anaerobic systems, so the probability of excessive biomass development in the system is much less. Table 25-41 summarizes the advantages and disadvantages of various combinations of reactor type, electron acceptor, and waste strength.

Recently, a new concept in fixed film reactors that uses an expanded or fluidized bed of particles as the biomass support medium has been introduced. This reactor type can easily handle both low- and high-strength wastes with most electron acceptors. It will be discussed in detail in a later section.

TABLE 25-41 Favorable (F) and Unfavorable (U) Combinations of Electron Acceptor, Waste Strength, and Reactor Type

Suspended growth reactor		
Electron acceptor	Waste strength	Condition
Aerobic	Low–modest	F
Aerobic	High	U
Anoxic	Low–modest	F
Anoxic	High	U
Anaerobic	Low–modest	U
Anaerobic	High	F
Fixed film reactor		
Electron acceptor	Waste strength	Condition
Aerobic	Low	F
Aerobic	Modest–high	U
Anoxic	Low–modest	F
Anoxic	High	U
Anaerobic	Low–modest	F
Anaerobic	High	F

Determination of Kinetic and Stoichiometric Pseudo Constants As indicated above, these parameters are most important for predicting the performance of biologically based treatment systems. It would be ideal if tabulations of these were available for various industrial wastes as a function of pH temperature and nutrient levels. Unfortunately, little reliable data has been codified. Only certain trends have been established, and these are primarily the result of studies on municipal wastewater. For example, the yield coefficient *Y* has been shown to be much higher for systems that are aerobic (molecular oxygen as the electron acceptor) than for anaerobic systems (sulfate or carbon dioxide as the electron acceptors). Systems where oxidized nitrogen is the electron acceptor (termed *anoxic*) exhibit yield values intermediate between aerobic and anaerobic systems. The endogenous respiration rate is higher for aerobic and anoxic systems than anaerobic systems. However, no trends have been established for values of the maximum specific growth rate or the half maximal velocity concentration. Thus, the values applicable to a specific waste must be determined from laboratory studies.

The laboratory studies utilized small-scale (1–5-L) reactors. These are satisfactory because the reaction rates observed are independent of reactor size. Several reactors are operated in parallel on the waste, each at a different BSRT. When steady state is reached after several weeks, data on the biomass level (*X*) in the system and the untreated waste level in the effluent (usually in terms of BOD or COD) are collected. These data can be plotted for equation forms that will yield linear plots on rectangular coordinates. From the intercepts and the slope of the lines, it is possible to determine values of the four pseudo constants. Table 25-42 presents some available data from the literature on these pseudo constants. Figure 25-53 illustrates the procedure for their determination from the laboratory studies discussed previously.

Activated Sludge This treatment process is the most widely used aerobic suspended growth reactor system. It will consistently produce a high-quality effluent (BOD_5 and SS of 20–30 mg/L). Operational costs are higher than for other secondary treatment processes primarily because of the need to supply molecular oxygen using energy-intensive mechanical aerator- or sparger-type equipment. Removal of soluble organics, colloidal, particulates, and inorganics are achieved in this system through a combination of biological metabolism, adsorption, and entrapment in the biological floc. Indeed, many pollutants that are not biologically degradable are removed during activated sludge treatment by adsorption or entrapment by the floc. For example, most heavy metals form hydroxide or carbonate precipitates under the pH conditions maintained in activated sludge, and most organics are easily adsorbed to the surface of the biological floc. A qualitative guide to the latter is provided by the octanol-water partition coefficient of a compound.

All activated sludge systems include a suspended growth reactor in which the wastewater, recycled sludge, and molecular oxygen are mixed. The latter must be dissolved in the water; thus the need for an energy-intensive pure oxygen or air supply system. Usually, air is the source of the molecular oxygen rather than pure oxygen. Energy for mixing of the reactor contents is supplied by the aeration equipment. All systems include a separator and pump station for sludge recycle and sludge wasting. The separator is usually a sedimentation tank that is designed to function as both a clarifier and a thickener. Many modifications of the activated sludge process have been developed over the years and are described below. Most of these involve differences in the way the reactor is compartmentalized with respect to introduction of waste, recycle, and/or oxygen supply.

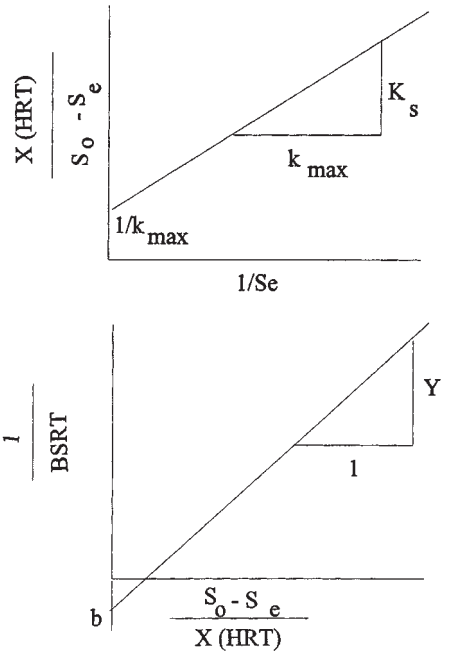


FIG. 25-53 Determination of pseudo-kinetic constants.

Modifications The modifications of activated sludge systems offer considerable choice in processes. Some of the most popular modifications of the activated sludge process are illustrated in Fig. 25-54. Conventional activated sludge uses a long narrow reactor with air supplied along the length of the reactor. The recycle sludge and waste are introduced at the head end of the reactor producing a zone of high waste to biomass concentration and high oxygen demand. This modification is used for relatively dilute wastes such as municipal wastewater. Step aeration systems distribute the waste along the length of the aerator, thus reducing the oxygen demand at the head end of the reactor and spreading the oxygen demand more uniformly over the whole reactor. In the complete mix system, the waste and sludge recycle are uniformly distributed over the whole reactor, resulting in the waste load and oxygen demand being uniform in the entire reactor. Complete-mixing activated sludge is the most popular system for industrial wastes because of its ability to absorb shock loads better than other modifications. Contact stabilization is a modification of activated sludge that is best suited to wastewaters having high suspended solids and low soluble organics. Contact stabilization employs a short-term mixing tank to adsorb the suspended solids and metabolize the soluble organics, a sedimentation tank for solids separation,

TABLE 25-42 Typical of Values for Pseudo Constants

Biomass type	Substrate	k_{max}, $\frac{\text{mg substrate}}{\text{mg biomass·day}}$	Y, $\frac{\text{mg biomass}}{\text{mg substrate}}$	K_s, $\frac{\text{mg substrate}}{\text{liter}}$	b, $\frac{1}{\text{day}}$	Remarks
Mixed culture	Sewage (COD)	5–10	0.5	50	0.05	Aerobic 20°C
Mixed culture	Glucose (COD)	7.5	0.6	10	0.07–.1	Aerobic 20°C
Mixed culture	Skim milk (COD)	5	—	100	0.05	Aerobic 20°C
Mixed culture	Soybean waste (COD)	12	—	355	0.144	Aerobic 20°C
Methane bacteria	Acetic acid (COD)	8.7	.04	165	0.035	35°C
Anaerobic mixed	Propanoic acid (COD)	7.7	.04	60	0.035	35°C
Anaerobic mixed	Sewage sludge (COD)	6.7	.04	1,800	0.03	35°C
Anoxic	NO_3 as N	0.375	0.8	0.1	0.04	Methanol feed
Aerobic	NH_4^+ as N	5	0.2	1.4	.05	20°C

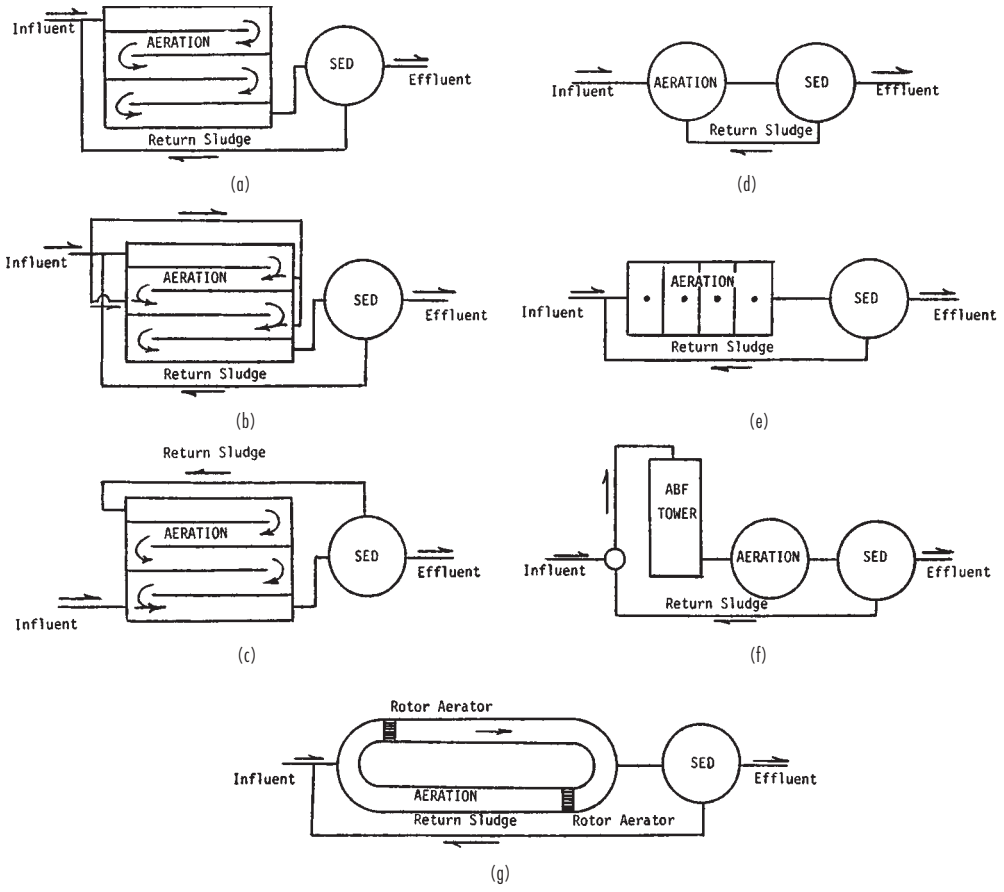


FIG. 25-54 Schematic diagrams of various modifications of the activated-sludge process. (*a*) Conventional activated sludge. (*b*) Step aeration. (*c*) Contact stabilization. (*d*) Complete mixing. (*e*) Pure oxygen. (*f*) Activated biofiltration (ABF). (*g*) Oxidation ditch.

and a reaeration tank for stabilization of the suspended organics. Extended-aeration systems are actually long-term-aeration, completely mixed activated-sludge systems. They employ 24- to 48-h aeration periods and high mixed-liquor suspended solids to provide complete stabilization of the organics and aerobic digestion of the activated sludge in the same aeration tank. The oxidation ditch is a popular form of the extended-aeration system employing mechanical aeration. Pure-oxygen systems are designed to treat strong industrial wastes in a series of completely mixed units having relatively short contact periods. One of the latest modifications of activated sludge employs powdered activated carbon to adsorb complex organics and assist in solids separation. Another modification employs a redwood-medium trickling filter ahead of a short-term aeration tank with mixed liquor recycled over the redwood-medium tower to provide heavy microbial growth on the redwood as well as in the aeration tank.

As indicated previously, success with the activated sludge process requires that the biomass have good self-flocculating properties. Significant research effort has been expended to determine the conditions that favor the development of good settling biomass cultures. These have indicated that nutritional deficiency, levels of dissolved oxygen between 0 to 0.5 mg/L, and pH values below 6.0 will favor the predomination of filamentous biomass. Filamentous organisms settle and compact poorly and thus are difficult to separate from liquid. By avoiding the above conditions, and with the application of selector technology, the predomination of filaments in the biomass can be eliminated. A selector is often a short contact (15–30 min) reactor set ahead of the main activated sludge reactor. All of the recycle sludge and all of the waste are routed to the selector. In the selector, either a high rate of aeration (aerobic selector) is used to keep the dissolved oxygen above 2 mg/L, or no aeration occurs (anaerobic selector) so that the dissolved oxygen is zero. Because filamentous organisms are microaerophilic, they cannot predominate when the dissolved oxygen level is zero or high. The anaerobic selector not only selects in favor of nonfilamentous biomass but also fosters luxury uptake of phosphorous and is used in systems where phosphorous removal is desired.

Aeration Systems These systems control the design of aeration tanks. Aeration equipment has two major functions: mixing and oxygen transfer. Diffused-aeration equipment employs either a fixed-speed positive-displacement blower or a high-speed turbine blower for readily adjustable air volumes. Air diffusers can be located along one side of the aeration tank or spread over the entire bottom of the tank. They can be either fine-bubble or coarse-bubble diffusers. Fine-bubble diffusers are more efficient in oxygen transfer but require more extensive air-cleaning equipment to prevent them from clogging as a result of dirty air. Mechanical-surface-aeration equipment is more efficient than diffused-aeration equipment but is not as flexible. Economics has dictated the use of large-power aerators, but tank configuration has tended to favor the use of greater numbers of lower-power aerators. Oxidation ditches use horizontal rotor-type aerators. Mixing is a critical problem with mechanical-surface aerators since they are a point-source pump of limited capacity. Experience has indicated that bearings are a serious problem with mechanical-aeration equipment. Wave action generated within the aeration tank tends to produce lateral stresses on the bearings and has resulted in failures and increased

maintenance costs. Slow-speed mechanical-surface-aeration units present fewer problems than the high-speed mechanical-surface-aeration units. Deep tanks, greater than 3.0 m (10 ft), require draft tubes to ensure proper hydraulic flow through the aeration tank. Short-circuiting is one of the major problems associated with mechanical aeration equipment. Combined mechanical- and diffused-aeration systems have enjoyed some popularity for industrial-waste systems that treat variable organic loads. The mechanical mixers provide the fluid mixing with the diffused aeration varied for different oxygen-transfer rates.

Diffused-aeration systems transfer from 20 to 40 mg/(L O_2·h). Combined mechanical- and diffused-aeration systems can transfer up to 65 mg/(L O_2·h), while mechanical-surface aerators can provide up to 90 mg/(L O_2·h). Pure-oxygen systems can provide the highest oxygen-transfer rate, up to 150 mg/(L O_2·h). Aeration equipment must provide sufficient oxygen to meet the peak oxygen demand; otherwise, the system will fail to provide proper treatment. For this reason, the peak oxygen demand and the rate of transfer for the desired equipment determine the size of the aeration tank in terms of retention time. Economics dictates a balance between the size of the aeration tank and the size of the aeration equipment. As the cost of power increases, economics will favor constructing a larger aeration tank and smaller aerators. It is equally important to examine the hydraulic flow pattern around each aerator to ensure maximum efficiency of oxygen transfer. Improper spacing of aeration equipment can waste energy.

There is no standard aeration-tank shape or size. Aeration tanks can be round, square, or rectangular. Shallow aeration tanks are more difficult to mix than deeper tanks. Yet aeration-tank depths have ranged from 0.6 m (2 ft) to 18 m (60 ft). The oxidation-ditch systems tend to be shallow, while some high-rate diffused-aeration systems have used very deep tanks to provide more efficient oxygen transfer.

Regardless of the aeration equipment employed, oxygen-transfer rates must provide from 0.6 to 1.4 kg of oxygen/kg BOD_5 (0.6 to 1.4 lb oxygen/lb BOD_5) stabilized in the aeration tank for carbonaceous-oxygen demand. Nitrogen oxidation can increase oxygen demand at the rate of 4.3 kg (4.3 lb) of oxygen/kg (lb) of ammonia nitrogen oxidized. At low oxygen-transfer rates more excess activated sludge must be removed from the system than at high oxygen-transfer rates. Here again the economics of sludge handling must be balanced against the cost of oxygen transfer. The quantity of waste activated sludge will depend upon wastewater characteristics. The inert suspended solids entering the treatment system must be removed with the excess activated sludge. The soluble organics are stabilized by converting a portion of the organics into suspended solids, producing from 0.3 to 0.8 kg (0.3 to 0.8 lb) of volatile suspended solids/kg (lb) of BOD_5 stabilized. Biodegradable suspended solids in the wastewaters will result in destruction of the original suspended solids and their conversion to a new form. Depending upon the chemical characteristics of the biodegradable suspended solids, the conversion factor will range from 0.7 to 1.2 kg (0.7 to 1.2 lb) of microbial solids produced/kg (lb) of suspended solids destroyed. If the suspended solids produced by metabolism are not wasted from the system, they will eventually be discharged in the effluent. While considerable efforts have been directed toward developing activated-sludge systems which totally consume the excess solids, no such system has proved to be practical. The concept of total oxidation of excess sludge is fundamentally unsound and should be recognized as such.

A definitive determination of the waste sludge production and the oxygen requirement can be obtained using the pseudo constants referred to previously. The ultimate BOD in the waste will be accounted for by the sum of the oxidation and sludge synthesis (Eq. 25-20).

Thus:

$$\text{Waste BOD}_u = \text{Oxygen required} + \text{BOD}_u \text{ of sludge produced} \quad (25\text{-}20)$$

where: BOD_U of sludge $= (Y_{\text{net}})(1.42)(\text{Waste BOD}_U)$

$$Y_{\text{net}} = \frac{Y}{1 + b(\text{BSRT})}$$

1.42 = Factor converting biomass to oxygen units; i.e., $\text{BOD}_u \approx \text{COD}$

Sedimentation Tanks These tanks are an integral part of any activated-sludge system. It is essential to separate the suspended solids from the treated liquid if a high-quality effluent is to be produced. Circular sedimentation tanks with various types of hydraulic sludge collectors have become the standard secondary sedimentation system. Square tanks have been used with common-wall construction for compact design with multiple tanks. Most secondary sedimentation tanks use center-feed inlets and peripheral-weir outlets. Recently, efforts have been made to employ peripheral inlets with submerged-orifice flow controllers and either center-weir outlets or peripheral-weir outlets adjacent to the peripheral-inlet channel.

Aside from flow control, basic design considerations have centered on surface overflow rates, retention time, and weir overflow rate. Surface overflow rates have been slowly reduced from 33 $m^3/(m^2 \cdot day)$ [800 gal/(ft^2·day)] to 24 $m^3/(m^2 \cdot day)$ to 16 $m^3/(m^2 \cdot day)$ [600 gal/(ft^2·day) to 400 gal/(ft^2·day)] and even to 12 m^3 (m^2·day) [300 gal/(ft^2·day)] in some instances, based on average raw-waste flows. Operational results have not demonstrated that lower surface overflow rates improve effluent quality, making 33 $m^3/(m^2 \cdot day)$ [800 gal/(ft^2·day)] the design choice in most systems. Retention time has been found to be an important design factor, averaging 2 h on the basis of raw-waste flows. Longer retention periods tend to produce rising sludge problems, while shorter retention periods do not provide for good solids separation with high-return sludge flow rates. Effluent-weir overflow rates have been limited to 186 $m^3/(m \cdot day)$ [15,000 gal/(ft·day)] with a tendency to reduce the rate to 124 $m^3/(m \cdot day)$ [10,000 gal/(ft·day)]. Lower effluent-weir overflow rates are obtained by using dual-sided effluent weirs cantilevered from the periphery of the tank. Unfortunately, proper adjustment of dual-side effluent weirs has created more hydraulic problems than the weir overflow rate. Field data have shown that effluent quality is not really affected by weir overflow rates up to 990 $m^3/(m \cdot day)$ [80,000 gal/(ft·day)] or even 1240 $m^3/(m \cdot day)$ [100,000 gal/(ft·day)] in a properly designed sedimentation tank. A single peripheral weir, being easy to adjust and keep clean, appears to be optimal for secondary sedimentation tanks from an operational point of view.

Depth tends to be determined from the retention time and the surface overflow rate. As surface overflow rates were reduced, the depth of sedimentation tanks was reduced to keep retention time from being excessive. It was recognized that depth was a valid design parameter and was more critical in some systems than retention time. As mixed-liquor suspended-solids (MLSS) concentrations increase, the depth should also be increased. Minimum sedimentation-tank depths for variable operations should be 3.0 m (10 ft) with depths to 4.5 m (15 ft) if 3000 mg/L MLSS concentrations are to be maintained under variable hydraulic conditions. With MLSS concentrations above 4000 mg/L, the depth of the sedimentation tank should be increased to 6.0 m (20 ft). The key is to keep a definite freeboard over the settled-sludge blanket so that variable hydraulic flows do not lift the solids over the effluent weir.

Scum baffles around the periphery of the sedimentation tank and radial scum collectors are standard equipment to ensure that rising solids or other scum materials are removed as quickly as they form. Hydraulic sludge-collection tubes have replaced the center sludge well, but they have caused a new set of operational problems. These tubes were designed to remove the settled sludge at a faster rate than conventional sludge scrapers. To obtain good hydraulic distribution in the sludge-collection tubes, it was necessary to increase the rate of return sludge flow and decrease the concentration of return sludge. The higher total inflow to the sedimentation tank created increased forces that lifted the settled-solids blanket at the wall, causing loss of excessive suspended solids and lower effluent quality. Operating data tend to favor conventional secondary sedimentation tanks over hydraulic sludge-collection systems. Return-sludge rates normally range from 25 to 50 percent for MLSS concentrations up to 3300 mg/L. Most return-sludge pumps are centrifugal pumps with capacities up to 100 percent raw-waste flow.

Gravity settling can concentrate activated sludge to 10,000 mg/L, but hydraulic sludge-collecting tubes tend to operate best below 8,000 mg/L. The excess activated sludge can be wasted either from the return sludge or from a separate waste-sludge hopper near the center of the

tank. The low solids concentrations result in large volumes of waste activated sludge in comparison with primary sludge. Unfortunately, the physical characteristics of waste activated sludge prevent significant concentration without the expenditure of considerable energy. Gravity thickening can produce 2 percent solids, while air flotation can produce 4 percent solids concentration. Centrifuges are able to concentrate activated sludge from 10 to 15 percent solids, but the capture is limited. Vacuum filters can equal the performance of centrifuges if the sludge is chemically conditioned. Filter presses and belt-press filters can produce cakes with 15 to 25 percent solids. It is very important that the excess activated sludge formed in the aeration tanks be wasted on a regular basis; otherwise, effluent quality will deteriorate. Care should be taken to ensure that sludge-thickening systems do not control activated-sludge operations. Alternative sludge-handling provisions should be available during maintenance on sludge-thickening equipment. At no time should final sedimentation tanks be used for the storage of sludge beyond that required by daily operational variations.

Anaerobic/Anoxic Activated Sludge The activated sludge concept (i.e., suspended growth reactor) can be used for anaerobic or anoxic systems in which no oxygen or air is added to the reactor. An anoxic activated sludge is used for systems in which removal of nitrate is a goal or where nitrate is used as the electron acceptor. These systems (denitrification) will be successful if the nitrate is reduced to low levels in the reactor so that nitrate reduction to nitrogen gas does not take place in the clarifier-thickener. Nitrogen gas production in the clarifier will result in escape of biological solids with the effluent as nitrogen bubbles floating sludge to the clarifier surface. For nitrogen reduction, a source of organics (electron donor) is required. Any inexpensive carbohydrate can be effectively used for nitrate removal. Many systems utilize methanol as the donor because it is rapidly metabolized; others use the organics in sewage in order to reduce chemical costs. Nitrate reduction is invariably used as part of a system in which organics and nitrogen removal are goals. In such systems, the nitrogen in the waste is first oxidized to nitrate and then reduced to nitrogen gas. Figure 25-55 presents some flow sheets for such systems. Table 25-43 presents some design parameters for nitrate-reduction-activated sludge systems. Anaerobic activated sludge has been used for strong industrial wastes high in degradable organic solids. In these systems, a high rate of gasification takes place in the sludge separator so that a highly clarified effluent is usually not obtained. A vacuum degasifier is incorporated in such systems to reduce solids loss. Such systems have been used primarily with meat packing wastes that are warm, high in BOD and yield a high level of bicarbonate buffer as a result of ammonia release from protein breakdown. All of these conditions favor anaerobic processing. The use of this process scheme provides a high BSRT (15–30 days), usually required for anaerobic treatment, at a low HRT (1–2 days).

TABLE 25-43 Design Parameter for Nitrogen Removal

System	BSRT, d	HRT, h	*X*, mg/L	pH
Carbon removal†	2–5	1–3	1000–2000	6.5–8.0
Nitrification†	10–20	0.5–3	1000–2000	7.4–8.6
Denitrification†	1–5	0.2–2	1000–2000	6.5–7.0
Internal recycle°	10–40	8–20	2000–4000	6.5–8.0

°Total for all reactors
†Separate reactors

Lagoons Lagoons are low-cost, easy-to-operate wastewater-treatment systems capable of producing satisfactory effluents. Nominally, a lagoon is a suspended-growth no-recycle reactor with a variable degree of mixing. In lagoons in which mechanical or diffused aeration is used, mixing may be sufficient to approach complete mixing (i.e., solids maintained in suspension). In other types of lagoons, most solids settle and remain on the lagoon bottom, but some mixing is achieved as a result of gas production from bacterial metabolism and wind action. Lagoons are categorized as aerobic, facultative, or anaerobic on the basis of degree of aeration. Aerobic lagoons primarily depend on mechanical or diffused air supply. Significant oxygen supply is also realized through natural surface aeration. A facultative lagoon is dependent primarily on natural surface aeration and oxygen

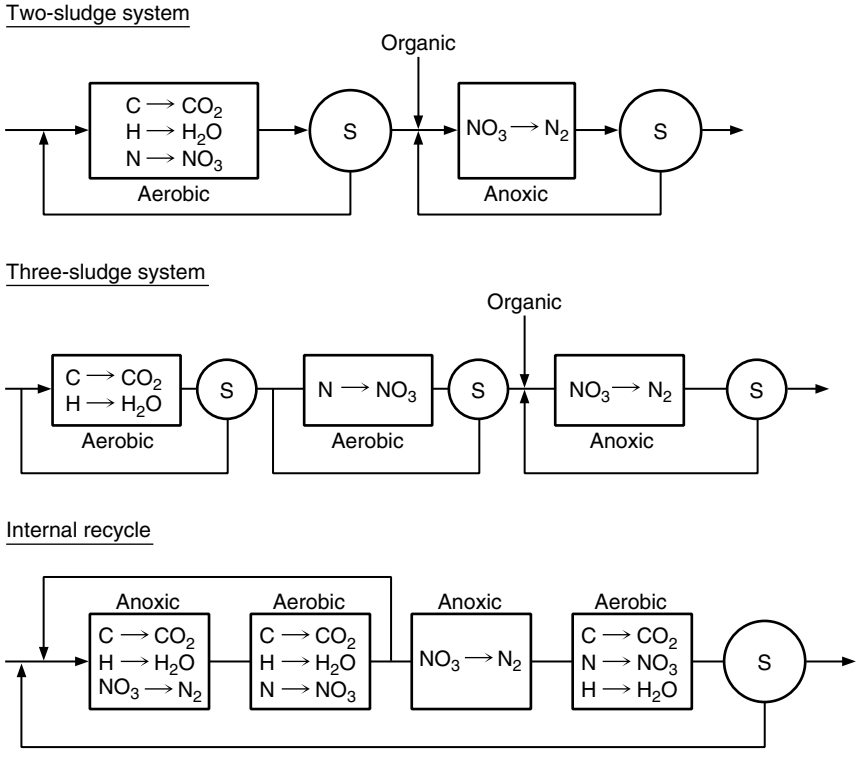


FIG. 25-55 Nitrogen removal systems.

generated by algal cells. These two lagoon types are relatively shallow to encourage surface aeration and provide for maximum algal activity. The third type of lagoon is maintained under anaerobic conditions to foster methane fermentation. This system is often covered with floating polystyrene panels to block surface aeration and help prevent a drop in temperature. Anaerobic lagoons are several meters deeper than the other two types. Lagoon flow schemes can be complex, employing lagoons in series and recycle from downstream to upstream lagoons. The major effect of recycle is to maintain control of the solids. If solids escape the lagoon system, a poor effluent is produced. Periodically controlled solids removal must take place or solids will escape.

Lagoons are, in effect, inexpensive reactors. They are shallow basins either cut below grade or formed by dikes built above grade or a combination of a cut and dike. The bottom must be lined with an impermeable barrier and the sides protected from wind erosion. These systems are best used where large areas of inexpensive land are available.

Facultative Lagoons These lagoons have been designed to use both aerobic and anaerobic reactions. Normally, facultative lagoons consist of two or more cells in series. The settleable solids tend to settle out in the first cell and undergo anaerobic metabolism with the production of organic acids and methane gas, which bubbles out to the atmosphere. Algae at the surface of the lagoon utilize sunlight for their energy in converting carbon dioxide, water, and ammonium ions into algal protoplasm with the release of oxygen as a waste product. Aerobic bacteria utilize the oxygen released by the algae to stabilize the soluble and colloidal organics. Thus, the bacteria and algae form a symbiotic relationship as shown in Fig. 25-56. The interesting aspect of facultative lagoons is that the organic matter in the incoming wastewaters is not stabilized but rather is converted to microbial protoplasm, which has a slower rate of oxygen demand. In fact, in some facultative lagoons inorganic compounds in the wastewaters are converted to organic compounds with a total increase in organics within the lagoon system.

Facultative lagoons are designed on the basis of organic load in relationship to the potential sunlight availability. In the northern part of the United States facultative lagoons are designed on the basis of 2.2 g/(m^2·day) [20 lb BOD_5/(acre·day)]. In the middle part of the United States the organic load can be increased to 3.4 to 4.5 g/(m^2·day) [30 to 40 lb BOD_5/(acre·day)], while in the southern part the organic load can be increased to 6.7 g/(m^2·day) [60 lb BOD_5/(acre·day)]. The depth of lagoons is normally maintained between 1.0 and 1.7 m (3 and 5 ft). A depth less than 1.0 m (3 ft) encourages the growth of aquatic weeds and permits mosquito breeding. In dry areas the maximum depth may be increased above 1.7 m (5 ft) depending upon evaporation. Most facultative lagoons depend upon natural wind action for mixing and should not be placed in screened areas where wind action is blocked.

Effluent quality from facultative lagoons is related primarily to the suspended solids created by living and dead microbes. The long retention period in the lagoons allows the microbes to die off, leaving a small particle that settles slowly. The release of nutrients from the dead microbes permits the algae to survive by recycling the nutrients.

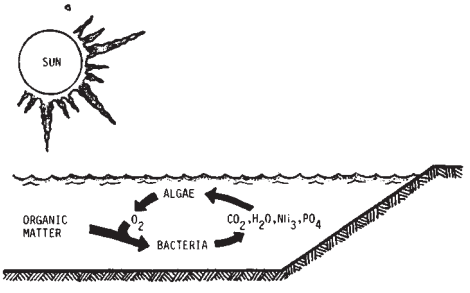


FIG. 25-56 Schematic diagram of oxidation-pond operations.

Thus, the algae determine the ultimate effluent quality. Use of series ponds with well-designed transfer structures between ponds permits maximum retention of algae within the ponds and the best-quality effluent. Normally the soluble BOD_5 is under 5 or 10 mg/L with a total effluent BOD_5 under 30 mg/L. The effluent suspended solids will vary widely during the different seasons of the year, being a maximum of 70 to 100 mg/L in the summer months and a minimum of 10 to 20 mg/L in the winter months. If suspended-solids removal is essential, chemical precipitation is the best method available at the present time. Slow sand filters and rock filters have been studied for suspended-solids removal; they work well as long as the effluent suspended solids are relatively low, 40 to 70 mg/L.

Aerated Lagoons These lagoons originated from efforts to control overloaded facultative lagoons. Since the lagoons were deficient in oxygen, additional oxygen was supplied by either mechanical surface aerators or diffused aerators. Mechanical surface aerators were quickly accepted as the primary aerators because they could be quickly added to existing ponds and moved to strategic locations. Unfortunately, the high-speed, floating surface aeration units were not efficient, and large numbers were required for existing lagoons. The problem was simply one of poor mixing in a very shallow lagoon.

Eventually, diffused aeration equipment was added to relatively deep lagoons [3.0 to 6.0 m (10 to 20 ft)]. Mixing became the most significant parameter for good oxygen transfer in aerated lagoons. From an economical point of view, it was found that a completely mixed aerated lagoon with 24-h retention provided the best balance between mixing and oxygen transfer. As the organic load increased, the fluid-retention time also increased. Short-term aeration permitted metabolism of the soluble organics by the bacteria, but time did not permit metabolism of the suspended solids. The suspended solids were combined with the microbial solids produced from metabolism and discharged from the aerated lagoon to a solids-separation pond. Data from the short-term aerated lagoon indicated that 50 percent BOD_5 stabilization occurred, with conversion of the soluble organics to microbial cells. The problem was separation and stabilization of the microbial cells. Short-term sedimentation ponds permitted separation of the solids without significant algae growths but required cleaning at frequent intervals to keep them from filling with solids and flowing into the effluent. Long-term lagoons permitted solids separation and stabilization but also permitted algae to grow and affect effluent quality.

Aerated lagoons were simply dispersed microbial reactors which permitted conversion of the organic components in the wastewaters to microbial solids without stabilization. The residual organics in solution were very low, less than 5 mg/L BOD_5. By adding oxygen and improving mixing, the microbial metabolism reaction was speeded up, but the stabilization of the microbial solids has remained a problem to be solved.

Anaerobic Lagoons These lagoons were developed when a major fraction of the organic contaminants consisted of suspended solids that could be removed easily by gravity sedimentation. The anaerobic lagoons are relatively deep [8.0 to 6.0 m (10 to 20 ft)], with a short fluid-retention time (3 to 5 days) and a high BOD_5 loading rate, up to 3.2 kg/(m^3·day) [200 lb/(1000 ft^3·day)]. Microbial metabolism in the settled-solids layer produces methane and carbon dioxide, which quickly rise to the surface, carrying some of the suspended solids. A scum layer that retards oxygen transfer and release of obnoxious gases is quickly produced in anaerobic lagoons. Mixing with a grinder pump can provide a better environment for metabolism of the suspended solids. The key for anaerobic lagoons is adequate buffer to keep the pH between 6.5 and 8.0. Protein wastes have proved to be the best pollutants to be treated by anaerobic lagoons, with the ammonium ions reacting with carbon dioxide and water to form ammonium bicarbonate as the primary buffer. High-carbohydrate wastes are poor in anaerobic lagoons since they produce organic acids without adequate buffer, making it difficult to maintain a suitable pH for good microbial growth.

Anaerobic lagoons do not produce a high-quality effluent but are able to reduce the BOD load by 80 to 90 percent with a minimum of effort. Since anaerobic lagoons work best on strong organic wastes, their effluent must be treated by either aerated lagoons or facultative

lagoons. An anaerobic lagoon is simply the first stage in the treatment of strong organic wastewaters.

Fixed Film Reactor Systems A major advantage of fixed film systems is that a flocculent-type biomass is not necessary as the biomass remains in the reactor attached to inert packing. Biomass does periodically slough off or break away from the packing, usually in large chunks that can be easily removed in a clarifier. On the other hand, the time of contact between the biomass and the waste is much shorter than in suspended growth systems, making it difficult to achieve the same degree of treatment especially in aerobic systems. Aerobic, anoxic, and anaerobic fixed film systems are utilized for waste treatment.

Aerobic systems including trickling filters and rotating biological contactors (RBC) are operated in a nonflooded mode to ensure adequate oxygen supply. Other aerobic, anoxic, and anaerobic systems employ flooded reactors. The most common systems are packed beds (anaerobic trickling filter) and fluidized or expanded bed systems.

Trickling Filters For years trickling filters were the mainstay of biological wastewater treatment systems because of their simplicity of design and operation. Trickling filters were displaced as the primary biological treatment system by activated sludge because of better effluent quality. Trickling filters are simply fixed-medium biological reactors with the wastewaters being spread over the surface of a solid medium where the microbes are growing. The microbes remove the organics from the wastewaters flowing over the fixed medium. Oxygen from the air permits aerobic reactions to occur at the surface of the microbial layer, but anaerobic metabolism occurs at the bottom of the microbial layer where oxygen does not penetrate.

Originally, the medium in trickling filters was rock, but rock has largely been replaced by plastic, which provides greater void space per unit of surface area and occupies less volume within the filter. A plastic medium permitted trickling filters to be increased from a medium depth of 1.8 m (6 ft) to one of 4.2 m (14 ft) and even 6.0 m (20 ft). The wastewaters are normally applied by a rotary distributor or a fixed-spray nozzle. The spraying or discharging of wastewaters above the trickling-filter medium permits better distribution over the medium and oxygen transfer before reaching the medium. The effluent from the trickling-filter medium is captured in a clay-tile underdrain system or in a tank below the plastic medium. It is important that the bottom of the trickling filter be open for air to move quickly through the filter and bring adequate oxygen for the microbial reactions.

If a high-quality effluent is required, trickling filters must be operated at a low hydraulic-loading rate and a low organic-loading rate. Low-rate trickling filters are operated at hydraulic loadings of 2.2×10^{-5} to 4.3×10^{-5} $m^3/(m^2 \cdot s)$ [2 million to 4 million gal/(acre·day)]. High-rate trickling filters are designed for 10.8×10^{-5} to 40.3×10^{-5} $m^3/(m^2 \cdot s)$ [10 million to 40 million gal/(acre·day)] hydraulic loadings and organic loadings up to 1.4 $kg/(m^3 \cdot day)$ [90 lb $BOD_5/(1000\ ft^3 \cdot day)$]. Plastic-medium trickling filters have been designed to operate up to 108×10^{-5} $m^3/(m^2 \cdot s)$ [100 million gal/(acre·day)] or even higher, with organic loadings up to 4.8 $kg/(m^3 \cdot day)$ [300 lb $BOD_5/(1000\ ft^3 \cdot day)$]. Low-rate trickling filters will produce better than 90 percent BOD_5 and suspended-solids reductions, while high-rate trickling filters will produce from 65 to 75 percent BOD_5 reduction. Plastic-medium trickling filters will produce from 59 to 85 percent BOD_5 reduction depending upon the organic-loading rate. It is important to recognize that concentrated industrial wastes will require considerable hydraulic recirculation around the trickling filter to obtain the proper hydraulic-loading rate without excessive organic loads. With high recirculation rates the organic load is distributed over the entire volume of the trickling filter for maximum organic removal. The short fluid-retention time within the trickling filter is the primary reason for the low treatment efficiency.

Rotating Biological Contactors (RBC) The newest form of trickling filter is the rotating biological contactor with a series of circular plastic disks, 3.0 to 3.6 m (10 to 12 ft) in diameter, immersed to approximately 40 percent diameter in a shaped contact tank. The RBC disks rotate at 2 to 5 r/min. As the disks travel through the wastewaters, a small layer adheres to them. As the disks travel into the air, the microbes on the disk surface oxidize the organics. Thus, only a small amount of energy is required to supply the required oxygen for wastewater treatment. As the microbes build up on the plastic disks, the shearing velocity that is created by the movement of the disks through the water causes the excess microbes to be removed from the disks and discharged to the final sedimentation tank.

Rotating biological contactors have been very popular in treating industrial wastes because of their relatively small size and their low energy requirements. Unfortunately, there have occurred a number of problems which should be recognized prior to using RBCs. Strong industrial wastes tend to create excessive microbial growths which are not easily sheared off and which create high oxygen-demand rates with the production of hydrogen sulfide and other obnoxious odors. The heavy microbial growths have damaged some of the disks and caused some shaft failures. The disks are currently being covered with plastic shells to prevent nuisance odors from occurring. Air must be forced through the covered RBC systems and be chemically treated before being discharged back into the environment. Recirculation of wastewater flow around the RBC units can distribute the load over all the units and reduce the heavy initial microbial growths. RBC units also work best under uniform organic loads, requiring surge tanks for many industrial wastes. The net result has been for the cost of RBC units to approach that of other treatment units in terms of organic matter stabilized.

RBCs should be designed on both a hydraulic-loading rate and an organic-loading rate. Normally, hydraulic-loading rates of up to 0.16 $m^3/(m^2 \cdot day)$ [4 $gal/(ft^2 \cdot day)$] of surface area are used with organic loading rates up to 44 $kg/(m^2 \cdot day)$ [9 lb $BOD_5/(ft^2 \cdot day)$]. Treatment efficiency is primarily a function of the fluid-retention time and the organic-loading rate. At low organic-loading rates the RBC units will produce nitrification in the same way as low-rate trickling filters.

Packed-Bed Fixed-Film Systems These systems were originally termed anaerobic trickling filters because the first systems were submerged columns filled with stones run under anaerobic conditions (Fig. 25-57). A wide variety of packed media is now used ranging in size from granules 40 mesh to 7.5-cm (3–in) stones. Many systems use open structure plastic packing similar to that used in aerobic trickling filters.

The systems using granular media packing are used for anoxic denitrification. They are usually downflow, thus serving the dual function of filtration and denitrification. Contact times are short (EBCT < 15 min), but excellent removal is achieved due to the high level of biomass retained in the reactor. Pacing the methanol dose to the varying feed nitrate concentration is crucial. Frequent, short-duration backwash (usually several times per day) is required or the nitrogen bubbles formed will bind the system, causing poor results. Extended backwash every two to three days is required or the system will clog on the biomass growth. Thus, several units in parallel or a large holding tank are needed to compensate for the down time during backwash. Backwash does not remove all the biomass; a thin film remains coating the packing. Thus, denitrification begins immediately when the flow is restored.

The systems using the larger packing are used in the treatment of relatively strong, low-suspended-solids industrial waste. These systems are closed columns usually run in an upflow mode with a gas space at the top. These are operated under anaerobic conditions with waste conversion to methane and carbon dioxide as the goal. Effluent recycle is often used to help maintain the pH in the inlet zone in the correct range 6.5–7.5 for the methane bacteria. Some wastes require the addition of alkaline material to prevent a pH drop. Sodium bicarbonate is often recommended for pH control because it is easier to handle than lime or sodium hydroxide, and because an overdose of bicarbonate will only raise the pH modestly. An overdose of lime or sodium hydroxide can easily raise the pH above 8.0. Table 25-44 gives some performance data with systems treating industrial wastes. HRTs of 1 to 2 days are used, as the buildup of growth on the packing ensures a BSRT of 20–50 days. It should be possible to lower the HRT further, but in practice this has not been successful because biomass starts to escape from the system or plugging occurs. Some escape is due to high gasification rates, and some is due to the fact that anaerobic sludge attaches less tenaciously to packing than aerobic or anoxic sludge. These systems can handle wastes with moderate solids levels. Periodically, solids must be removed from the reactor to prevent plugging of the packing or loss of solids in the effluent.

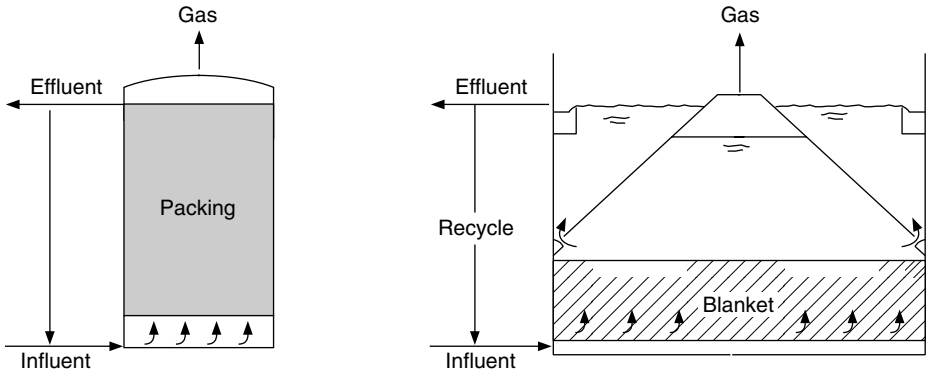


FIG. 25-57 Anaerobic processes.

Biological Fluidized Beds This high-rate process has been used successfully for aerobic, anoxic, and anaerobic treatment of municipal and industrial wastewaters. Numerous small- and large-scale applications for hazardous waste, contaminated groundwater, nontoxic industrial waste and municipal wastewater have been reported (Refs. 32 and 33). The basic element of the process is a bed of solid carrier particles, such as sand or granular activated carbon, placed in a reactor through which wastewater is passed upflow with sufficient velocity to impart motion or fluidize the carrier. An active growth of biological organisms grow as firmly attached mass surrounding each of the carrier particles. As the wastewater contaminants pass by the biologically covered carrier, they are removed from the wastewater through biological and adsorptive mechanisms. Figure 25-58 is a schematic of the process.

The influent wastewater enters the reactor through a pipe manifold and is introduced downflow through nozzles that distribute the flow uniformly at the base of the reactor. Reversing direction at the bottom, the flow fluidizes the carrier when the fluid drag overcomes the buoyant weight of the carrier and its attached biomass layer. During startup (before much biomass has accumulated), the flow velocity required to achieve fluidization is higher than after the biomass attaches. Recycle of treated effluent is adjusted to achieve the desired degree of fluidization. As biomass accumulates, the particles of coated biomass will separate to a greater extent at constant flow velocity. Thus, as the system ages and more biomass accumulates, the extent of bed expansion increases (the volume of voids increases). This phenomenon is advantageous because it prevents clogging of the bed with biomass. Consequently, higher levels of biomass attachment are possible than in other types of fixed film systems. However, eventually, the degree of bed expansion may become excessive. Reduction of recycle will reduce expansion but may not be feasible because recycle has several purposes (i.e., supply of nutrients, alkalinity, and dilution of waste strength). Control of the expanded bed surface level is automatically accomplished using a sensor that activates a biomass growth control system at a prescribed level and maintains the bed at the proper depth. A pump removes a portion of the attached biomass, separates the biomass and inert carrier by abrasion, and pumps the mixture into a separator. Here the heavy carrier settles back into the fluidized bed and the abraded biomass, which is less dense, is removed from the system by gravity or a second pump. Other growth control designs are also used. Effluent is withdrawn from the supernatant layer above the fluidized bed. The reactor is usually not covered unless it is operating under anaerobic conditions and methane, odorous gases, or other safety precautions are mandated.

When aerobic treatment is to be provided to high concentrations of organics, pure oxygen or hydrogen peroxide may be injected into the wastewater prior to entering the reactor. Liquid oxygen (LOX) or pressure swing absorption (PSA) systems have been used to supply oxygen. Air may be used at low D.O. demands.

In full-scale applications, this process has been found to operate at significantly higher volumetric loading rates for wastewater treatment than other processes. The primary reasons for the very high rates of contaminant removal is the high biologically active surface area available (approximately 1000 ft^2/ft^3 of reactor) and the high concentration of reactor biological solids (8,000–40,000 mg/L) that can be maintained (Table 25-45). Because of these atypical high values, designs usually indicate a 200–500 percent reduction in reactor volume when compared to other fixed film and suspended growth treatment processes. In Table 25-46, is a list of full-scale commercial applications of the process operated at high wastewater concentrations including

TABLE 25-44 Anaerobic Process Performance on Industrial Wastewater UASB, Submerged filter (SF), FBR

Process	Wastewater	Reactor size, MG	COD, g/l	OVL, kg/m^3d	%CODr	HRT-d	°C
SF	Rum slops	3.5	80–105	15	71	7.8	35
SF	Modified guar	0.27	9.1	7.5	60	1.0	37
SF	Chemical	1.5	14	11	90	0.7	H
SF	Milk	0.2	3	7.5	60	0.5	32
SF	PMFC	10^{-5}	13.7	23	72	0.6	36
UASB	Potato	0.58	2.5	3	85	0.7	35
UASB	Sugar beet	0.21	3	16	88	—	—
UASB	Brewery	1.16	1.6–2.2S	4.4	83	0.4	30
UASB	Brewery	1.16	2.0–2.4S	8.7	78	0.2	30
UASB	PMFC	10^{-5}	13.7	4–5	87	2.9	36
FBR	PMFC	10^{-5}	13.7	35–48	88	0.4	36
FBR	Soft drink	0.04	3.0	6–7	75	0.5	35
FBR	Chemical	0.04	35	14	95	2.5	35

OVL = organic volumetric load (COD)
S = settled effluent
H = heated
PMFC = paper mill foul condensate (5,6)
NOTE: MG = 3785 m^3.

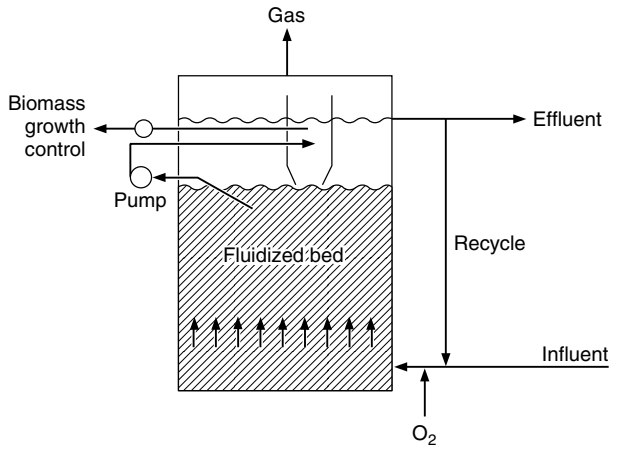


FIG. 25-58 Schematic of fluidized bed process.

aerobic oxidation of organics, anoxic denitrification and anaerobic treatment systems.

Of special note is the enhancement to the process when granular activated carbon (GAC) is used as the carrier. Because GAC has adsorptive properties, organic compounds present in potable waters and wastewater at low concentrations, often less than ten mg/L, are removed by adsorption and subsequently consumed by the biological organisms that grow in the fluidized bed. The BTEX compounds, methylene chloride, chlorobenzene, plastics industry toxic effluent, and many others are removed in this manner. BTEX contamination of groundwater from leaking gasoline storage tanks is a major problem, and sixteen full-scale fluidized bed process applications have been made. Contaminated groundwater is pumped to the ground surface for treatment using the fluidized bed in the aerobic mode. Often the level of BTEX is 1–10 mg/L and about 99 percent is removed in less than ten minutes detention time. Installations in operation range in size from 30 to 3000 gpm. The smaller installations are often skid-mounted and may be moved from location to location at a given site. A major advantage of this process over stripping towers and vacuum systems for treating volatile organics (VOCs) is the elimination of effluent gas treatment.

Also, pilot plant and laboratory scale anaerobic studies have demonstrated successful treatment of wastewaters of 5,000 to 50,000 mg/L COD from corn chips containing soluble and colloidal corn starch and protein, cheese whey, organic chemicals, food, bakery, brewery, paper mill foul condensate, paint, and numerous other hazardous and nonhazardous materials.

Design criteria for satisfactory biological fluidized bed treatment systems include the major parameters given in Table 25-47.

Earlier the anaerobic trickling filter was discussed and in the above section the fluidized bed reactor was reviewed. A third type of reactor system with some similarity is the upflow anaerobic sludge blanket (UASB) system. Here, a flocculent biomass is retained in the reactor with no recycle of sludge necessary. The sludge is maintained in the system by the use of a relatively low flow rate. The sludge formed seems to be granular in nature and has a relatively high specific gravity. It is thought that the presence of small particles of $CaCO_3$ and/or clay in the waste may contribute to the formation of the dense sludge. A diagram of this system is shown in Fig. 25-56. The supplier of this system provides a startup seed of this granular-type biomass.

The anaerobic filter, UASB, and fluidized bed reactors have all been used for anaerobic treatment of industrial wastes, as each is especially suited for use in anaerobic treatment. Table 25-44 presents results from these applications.

TABLE 25-45 Process Comparisons

Biological process	MLVSS, mg/L	Surface area, ft^2/ft^3
Activated sludge	1500–3000	—
Pure oxygen activated sludge	2000–5000	—
Suspended growth nitrification	1000–2000	—
Suspended growth denitrification	1500–3000	—
Fluidized bed-CBOD removal	12,000–20,000	800–1200
Fluidized bed-nitrification	8,000–12,000	800–1200
Fluidized bed-denitrification	25,000–40,000	800–1200
Trickling filter-CBOD removal	—	12–50
RBC-CBOD removal	—	30–40

TABLE 25-46 Full-Scale Commercial Applications of Fluidized Bed Process

Application	Type	Reactor volume, m^3
CBOD—paint—General Motors	Aerobic	108
C,NBOD—sanitary and automotive—GM	Aerobic	165
Chemical—Grindsted Products Denmark	Aerobic	730
Nitrification—fish hatchery—Idaho	Aerobic	820
BTEX, groundwater—Ohio	Aerobic	250
Chemical, Toxicity reduction—Texas	Aerobic	225
Denitrification, Nuclear Fuel, DOE, Fornald, OH	Anoxic	53
CBOD, Denitrification—municipal, Nevada	Anoxic	1450
Petrochemical—Reliance Ind. India	Anaerobic	850
Soft drink, Delaware	Anaerobic	166
Brewery—El Aguila, Spain	Anaerobic	1570

PHYSICAL-CHEMICAL TREATMENT

Processes and/or unit operations that fall under this classification include adsorption, ion exchange, stripping, chemical oxidation, and membrane separations. All of these are more expensive than biological treatment but are used for removal of pollutants that are not easily removed by biomass. Often these are utilized in series with biological treatment; but sometimes they are used as stand-alone processes.

Adsorption This is the most widely used of the physical-chemical treatment processes. It is used primarily for the removal of soluble organics with activated carbon serving as the adsorbent. Most liquid-phase-activated carbon adsorption reactions follow a Freundlich Isotherm [Eq. (25-21)].

$$y = kc^{1/n} \tag{25-21}$$

where: y = adsorbent capacity, mass pollutant/mass carbon
c = concentration of pollutant in waste, mass/volume
k and n = empirical constants

EPA has compiled significant data on values of k and n for environmentally significant pollutants with typical activated carbons. Assuming equilibrium is reached, the isotherm provides the dose of carbon required for treatment. In a concurrent contacting process, the capacity is set by the required effluent concentration. In a countercurrent process, the capacity of the carbon is set by the untreated waste pollutant concentration. Thus countercurrent contacting is preferred.

Activated carbon is available in powdered form (200–400 mesh) and granular form (10–40 mesh). The latter is more expensive but is easier to regenerate and easier to utilize in a countercurrent contactor. Powdered carbon is applied in well-mixed slurry-type contactors for

TABLE 25-47 Typical Design Parameters for Fluidized Beds

Waste	Mode	Influent concentration, mg/L	Volumetric load, $lb/ft^3 \cdot d$	Hydraulic detention time, hr	Volatile solids (biosolids), g/L
Organic COD	Aerobic	<2000	0.1–0.6	0.5–2.5	12–20
Organic COD	Aerobic	<10	0.02–0.1	0.1–0.5	4–8
NH_3-N	Aerobic	<25	0.05–0.3	0.1–0.5	7–14
NO_3^--N	Anoxic	<5,000	0.4–2	0.1–2.4	20–40
Organic COD	Anaerobic	>4000	0.5–4	2–24	20–40

NOTE: $lb/ft^3 \cdot d = 16\ kg/m^3 \cdot d$.

detention times of several hours after which separation from the flow occurs by sedimentation. Often coagulation, flocculation, and filtration are required in addition to sedimentation. As it is difficult to regenerate, powdered carbon is usually discarded after use. Granular carbon is used in column contactors with EBCT of 30 minutes to 1 hour. Often several contactors are used in series, providing for full countercurrent contact. A single contactor will provide only partial countercurrent contact. When a contactor is exhausted, the carbon is regenerated either by a thermal method or by passing a solvent through the contactor. For waste-treatment applications where a large number of pollutants must be removed but the quantity of each pollutant is small, thermal regeneration is favored. In situations where a single pollutant in large quantity is removed by the carbon, solvent extraction regeneration can be used, especially where the pollutant can be recovered from the solvent and reused. Thermal regeneration is a complex operation. It requires removal of the carbon from the contactor, drainage of free water, transport to a furnace, heating under controlled conditions of temperature, oxygen, time, water vapor partial pressure, quenching, transport back to the reactor, and reloading of the column. Five to ten percent of the carbon is lost in this regeneration process due to burning and attrition during each regeneration cycle. Multiple hearth, rotary kiln, and fluidized bed furnaces have all been successfully used for carbon regeneration.

Pretreatment prior to carbon adsorption is usually for removal of suspended solids. Often this process is used as tertiary treatment after primary and biological treatment. In either situation, the carbon columns must be designed to provide for backwash. Some solids will escape pretreatment, and biological growth will occur on the carbon, even with extensive pretreatment. Originally carbon treatment was viewed only as applicable for removal of toxic organics or those that are difficult to degrade biologically. Present practice applies carbon adsorption as a procedure for removal of all types of organics. It is realized that some biological activity will occur in virtually any activated carbon unit, so the design must be adjusted accordingly.

Ion Exchange This process has been employed for many years for treatment of industrial water supplies but not for wastes. However, some new ion-exchange materials have recently been developed that can be used for removal of specific pollutants. These new resins are primarily useful for selective removal of heavy metals, even though the target metals are present at low concentration in a wastewater containing many other inorganics. An ion-exchange process is usually operated with the waste being run downflow through a series of columns containing the appropriate ion-exchange resins. EBCT contact times of 30 min to 1 hour are used. Pretreatment for suspended solids and organics removal is practiced as well as pH adjustment.

The capacity of an ion-exchange resin is a function of the type and concentration of regenerant. Because ion-exchange resins are so selective for the target compound, a significant excess of the regenerant must be used. Up to a point, the more regenerant, the greater the capacity of the resin. Unfortunately, this results in waste of most of the regenerant. In fact, the bulk of the operational cost for this process is for regenerant purchase and its disposal; thus, regeneration must be optimized. Regenerants used (selection depends on the ion exchange resin) include sodium chloride, sodium carbonate, sulfuric acid, sodium hydroxide, and ammonia. Table 25-48 gives information on some of the new highly selective resins. These resins may provide the only practical method for reduction of heavy metals to the very low levels required by recent EPA regulations.

Stripping Air stripping is applied for the removal of volatile substances from water. Henry's law is the key relationship for use in design of stripping systems. The minimum gas-to-liquid ratio required for stripping is given by:

$$\frac{G}{L} = \frac{S_{in} - X_{out}}{(H)X_{out}}$$

for a concurrent process and

$$\frac{G}{L} = \frac{X_{in} - X_{out}}{(H)X_{in}}$$

for a countercurrent process where:

G = air flow rate, mass/time
L = waste flow rate, volume/time
X = concentration of pollutant in waste, mass/volume
H = Henry's constant for the pollutant in water, volume/mass

Higher ratios of gas to liquid flow are required than those computed above because mass-transfer limitations must be overcome. Stripping can occur by sparging air into a tank containing the waste. Indeed, stripping of organics from activated sludge tanks is of concern because of the possibility that the public will be exposed to airborne pollutants including odors. A much more efficient stripping procedure is to use counterflow or crossflow contact towers. Procedures for design of these and mass-transfer characteristics of various packings are available elsewhere in this handbook.

Stripping has been successfully and economically employed for removal of halogenated organics from water and wastes with dispersion of the effluent gas to the atmosphere. However, recent EPA regulations have curtailed this practice. Now removal of these toxic organics from the gas stream is also required. Systems employing activated carbon (prepared for use with gas streams) are employed as well as systems to oxidize the organics in the gas stream. However, the cost of cleaning up the gas stream often exceeds the cost of stripping these organics from the water.

Chemical Oxidation This process has not been widely utilized because of its high cost. Only where the concentration of the target compound is very low will the quantity of oxidant required be low enough to justify treatment by chemical oxidation. The efficiency of this process is also low, as many side reactions can occur that will consume the oxidant. In addition, complete oxidation of organics to carbon dioxide and water often will not occur unless a significant overdose is used. However, renewed interest has recently occurred for two reasons.

1. It has been found that partial oxidation is satisfactory as a pretreatment to biological or carbon adsorption treatment. Partial oxidation often seems to make recalcitrant organics easier to degrade biologically and easier to adsorb.
2. A combination of ozone oxidation with simultaneous exposure to ultraviolet light seems to produce a self-renewing chain reaction that can significantly reduce the dose of ozone needed to accomplish oxidation.

Oxidants commonly used include ozone, permanganate, chlorine, chlorine dioxide, and ferrate, often in combination with catalysts. Standard-type mixed reactors are used with contact times of several minutes to an hour. Special reactors for use with ultraviolet light have been developed.

Membrane Processes These processes use a selectively permeable membrane to separate pollutants from water. Most of the mem-

TABLE 25-48 Selective Ion-Exchange Resins

Application	Exchanger type	Composition	Regenerant
Softening	Cation	Polystyrene matrix Sulfonic acid functional groups	NaCl
Heavy metals	Cation	Polystyrene matrix Chelating functional groups	Mineral acids
Chromate	Anion	Polystyrene matrix Tertiary or quaternary ammonium functional groups	Sodium carbonate or alkaline NaCl
Nitrate	Anion	Polystyrene matrix Tributyl ammonium functional group	NaCl

branes are formulated from complex organics that polymerize during membrane preparation. This allows the membrane to be tailored to discriminate by molecular size or by degree of hydrogen bonding potential. Ultrafiltration membranes discriminate by molecular size or weight, while reverse osmosis membranes discriminate by hydrogen-bonding characteristics. The permeability of these membranes is low: from 0.38–3.8 m/day (10–100 gal/d/ft^2). The apparatus in which they are used must provide a high surface area per unit volume. The membranes are also fragile and are often subjected to several hundred psi of pressure. Thus the apparatus must provide a rugged support structure and efficient seals to prevent leakage. Membrane support configurations include tubular, spiral-wound, and hollow fine fiber systems. An operational problem is the buildup of pollutant on the side of the membrane where rejection occurs. This leads to fouling of the membrane surface which initially reduces water flux. Eventually, deterioration and membrane failure occur. Membrane life is in the range 1–2 years. New membrane materials with improved properties are being sought. Membrane separation-based systems require extensive pretreatment and continual maintenance to reduce fouling. These systems have significant potential, but much developmental work is needed on membrane characteristics and the support apparatus.

SLUDGE PROCESSING

Objectives Sludges consist primarily of the solids removed from liquid wastes during their processing. Thus, sludges could contain a wide variety of pollutants and residuals from the application of treatment chemicals; i.e., large organic solids, colloidal organic solids, metal sulfides, heavy-metal hydroxides and carbonates, heavy-metal organic complexes, calcium and magnesium hydroxides, calcium carbonate, precipitated soaps and detergents, and biomass and precipitated phosphates. As sludge even after extensive concentration and dewatering is still greater than 50 percent by weight water, it can also contain soluble pollutants such as ammonia, priority pollutants, and nonbiologically degradable COD.

The general treatment or management of sludge involves stabilization of biodegradable organics, concentration and dewatering, and ultimate disposal of the stabilized and dewatered residue. A large number of individual unit processes and unit operations are used in a sludge-management scheme. Those most frequently used are discussed below. Occasionally, only one of these is needed, but usually several are used in a series arrangement.

Because of the wide variability in sludge characteristics and the variation in acceptability of treated sludges for ultimate disposal (this is a function of the location and characteristics of the ultimate disposal site), it is impossible to prescribe any particular sludge-management plan. In the sections below, general performance of individual sludge-treatment processes and operations is presented.

Concentration: Thickening and Flotation Generated sludges are often dilute (1–2 percent solids by weight). In order to reduce the volumetric loading on other processes, the first step in sludge processing is often concentration. The most popular process is gravity thickening which is carried out in treatment units similar to circular clarifiers. Organic sludges from primary treatment can usually be concentrated to 5–8 percent solids. Sludges from secondary treatment can be thickened to 2 percent solids. The potential concentration with completely inorganic sludges is higher (greater than 10 percent solids) except for sludges high in metal hydroxides. Polymers are often used to speed up thickening and increase concentration. Thickening is enhanced by long retention of the solids in the thickening apparatus. However, when biodegradable organics are present, solids retention time must be at a level that will not foster biological activity, lest odors, gas generation, and solids hydrolysis occur. Loading rates on thickeners range from 50–122 kg/m^2/d (10–25 lb/ft^2/d) for primary sludge to 12–45 kg/m^2/d (2.5–9 lb/ft^2/d). Solids detention time is 0.5 days in summer to several days in winter.

Flotation Air flotation has proved to be successful in concentrating secondary sludges to about 4 percent solids. The incoming solids are normally saturated with air at 275 to 350 kPa (40 to 50 psig) prior to being released in the flotation tank. As the air comes out of solution, the fine bubbles are trapped under the suspended solids and carry them to the surface of the tank. The air bubbles compact the solids as a floating mass. Normally, the air-to-solids ratio is about 0.01–0.05 L/g (0.16–0.8 ft^3/lb). The thickened solids are scraped off the surface, while the effluent is drawn off the middle of the tank and returned to the treatment system. In large flotation tanks with high flows the effluent rather than the incoming solids is pressurized and recycled to the influent. The size of the flotation tanks is determined primarily by the solids-loading rate, directly or indirectly. A solids loading of 25 to 97 kg/(m^2·day) [5 to 20 lb/(ft^2·day)] has been found to be adequate. On a flow basis this translates into 0.14 to 2.7 L/(m^2·day) [0.2 to 4 gal/(ft^2·min)] surface area.

As with thickening, air flotation is enhanced by the addition of polymers. Flotation has been successfully used with wholly inorganic metal hydroxide sludges. Polymers and surfactants are used as additives. Engineering details on air flotation equipment has been developed by and is available from various equipment manufacturing companies. Liquid removed during thickening and flotation is usually returned to the head end of the plant.

Stabilization (Anaerobic Digestion, Aerobic Digestion, High Lime Treatment) Sludges high in organics can be stabilized by subjecting them to biological treatment. The most popular system is anaerobic digestion.

Anaerobic Digestion Anaerobic digesters are large covered tanks with detention times of 30 days, based on the volume of sludge added daily. Digesters are usually heated with an external heat exchanger to 35–37° C to speed the rate of reaction. Mixing is essential to provide good contact between the microbes and the incoming organic solids. Gas mixing and mechanical mixers have been used to provide mixing in the anaerobic digester. Following digestion, the sludge enters a holding tank, which is basically a solids-separation unit and is not normally equipped for either heating or mixing. The supernatant is recycled back to the treatment plant, while the settled sludge is allowed to concentrate to 3–6 percent solids before being further processed.

Anaerobic digestion results in the conversion of the biodegradable organics to methane, carbon dioxide, and microbial cells. Because of the energy in the methane, the production of microbial mass is quite low, less than 0.1 kg/kg (0.1 lb volatile suspended solids (VSS)/lb) BCOD metabolized except for carbohydrate wastes. The production of methane is 0.35 m^3/kg (5.6 ft^3/lb) BCOD destroyed. Digester gases range from 50 to 80 percent methane and 20 to 50 percent carbon dioxide, depending on the chemical characteristics of the waste organics being digested. The methane is often used on site for heat and power generation.

There are three major groups of bacteria that function in anaerobic digestion. The first group hydrolyzes large soluble and nonsoluble organic compounds such as proteins, fats and oils (grease), and carbohydrates, producing smaller water-soluble compounds. These are then degraded by acid-forming bacteria, producing simple volatile organic acids (primarily acetic acid) and hydrogen. The last group (the methane bacteria) split acetic acid to methane and carbon dioxide and produce methane from carbon dioxide and hydrogen. Good operation requires the destruction of the volatile acids as quickly as they are produced. If this does not occur, the volatile acids will build up and depress the pH, which will eventually inhibit the methane bacteria. To prevent this from occurring, feed of organics to the digester should be as uniform as possible.

If continuous addition of solids is not possible, additions should be made at as short intervals as possible. Alkalinity levels are normally maintained at about 3000 to 5000 mg/L to keep the pH in the range 6.5–7.5 as a buffer against variable organic-acid production with varying organic loads. Proteins will produce an adequate buffer, but carbohydrates will require the addition of alkalinity to provide a sufficient buffer. Sodium bicarbonate should be used to supply the buffer.

An anaerobic digester is a no-recycle complete mix reactor. Thus, its performance is independent of organic loading but is controlled by hydraulic retention time (HRT). Based on kinetic theory and values of the pseudo constants for methane bacteria, a minimum HRT of 3 to 4 days is required. To provide a safety factor and compensate for load variation as indicated earlier, HRT is kept in the range 10 to 30 days. Thickening of feed sludge is used to reduce the tank volume required

to achieve the long HRT values. When the sludge is high in protein, the alkalinity can increase to greater than 5000 mg/L, and the pH will rise past 7.5. This can result in free ammonia toxicity. To avoid this situation, the pH should be reduced below 7.5 with hydrochloric acid. Use of nitric or sulfuric acid will result in significant operational problems.

Aerobic Digestion Waste activated sludge can be treated more easily in aerobic treatment systems than in anaerobic systems. The sludge has already been partially aerobically digested in the aeration tank. For the most part, only about 25 to 35 percent of the waste activated sludge can be digested. An additional aeration period of 15 to 20 days should be adequate to reduce the residual biodegradable mass to a satisfactory level for dewatering and return to the environment. One of the problems in aerobic digestion is the inability to concentrate the solids to levels greater than 2 percent. A second problem is nitrification. The high protein concentration in the biodegradable solids results in the release of ammonia, which can be oxidized during the long retention period in the aerobic digester. Limiting oxygen supply to the aerobic digester appears to be the best method to handle nitrification and the resulting low pH.

A new concept is to use an on/off air supply cycle. During aeration, nitrates are produced. When the air is shut off, nitrates are reduced to nitrogen gas. This prevents acid buildup and removes nitrogen from the sludge. High power cost for aerobic digestion restricts the applicability of this process.

High Lime Treatment Uses doses of lime sufficient to raise the pH of sludge to 12 or above. As long as the pH is maintained at this level, biological breakdown will not occur. In this sense, the sludge is stable. However, any reduction of pH as a result of contact with CO_2 in the air will allow biological breakdown to begin. Thus, this technique should only be used as temporary treatment until further processing can occur. It is not permanent stabilization as is provided by anaerobic or aerobic digestion.

Sludge Dewatering Dewatering is different from concentration in that the latter still leaves a substance with the properties of a liquid. The former produces a product which is essentially a friable solid. When the water content of sludge is reduced to <70–80 percent, it forms a porous solid called sludge cake. There is no free water in the cake, as the water is chemically combined with the solids or tightly adsorbed on the internal pores. The operations below which are used to dewater sludge can be applied at any stage of the sludge management process, but often they follow concentration and/or biological stabilization. Chemical conditioning is almost always used to aid dewatering.

Lime, alum, and various ferric salts have been used to condition sludge prior to dewatering. Lime reacts to form calcium carbonate crystals, which act as a solid matrix to hold the sludge particles apart and allow the water to escape during dewatering. Alum and iron salts help displace some of the bound water from hydrophilic organics and form part of the inorganic matrix. Chemical conditioning increases the mass of sludge to be ultimately handled from 10 to 25 percent, depending upon the characteristics of the individual sludge. Chemical conditioning can also help remove some of the fine particles by incorporating them into insoluble chemical precipitates. The water (supernatant) removed from the sludge during dewatering is often high in suspended solids and organics. Addition of polymers prior to, during, or after dewatering will often reduce the level of pollutants in the supernatant.

Centrifugation Both basket and solid-bowl centrifuges have been used to concentrate waste sludges. Field data have shown that it is possible to obtain 10 to 20 percent solids with waste activated sludge, 15 to 30 percent solids with a mixture of primary and waste activated sludge, and up to 30 to 35 percent solids with primary sludge alone. Centrifuges result in 85 to 90 percent solids capture with good operation. The problem is that the centrate contains the fine solids not easily removed. The centrate is normally returned to the treatment process, where it may or may not be removed. Economics do not favor centrifuges unless the sludge cake produced is at least 25 to 30 percent solids. For the most part, centrifuges are designed by equipment manufacturers from field experience. With varying sludge characteristics centrifuge characteristics will also vary widely.

Vacuum Filtration Vacuum filtration has been the most common method employed in dewatering sludges. Vacuum filters consist of a rotary drum covered with a cloth-filter medium. Various plastic fibers as well as wool have been used for the filter cloth. The filter operates by drawing a vacuum as the drum rotates into chemically conditioned sludge. The vacuum holds a thin layer of sludge, which is dewatered as the drum rotates through the air after leaving the vat. When the drum rotates the cloth to the opposite side of the apparatus, air-pressure jets replace the vacuum, causing the sludge cake to separate from the cloth medium as the cloth moves away from the drum. The cloth travels over a series of rollers, with the sludge being separated by a knife edge and dropping onto a conveyor belt by gravity. The dewatered sludge is moved on the conveyor belt to the next concentration point, while the filter cloth is spray-washed and returned to the drum prior to entering the sludge vat. Vacuum filters yield the poorest results on waste activated sludge and the best results on primary sludge. Waste activated sludge will concentrate to between 12 and 18 percent solids at a rate of 4.9 to 9.8 kg dry cake/(m^2·h) [1 to 2 lb/(ft^2·h)]. Primary sludge can be dewatered to 25 to 30 percent solids at a rate of 49 kg dry cake/(m^2·h) [10 lb/(ft^2·h)].

Pressure Filtration Pressure filtration has been used increasingly since the early 1970s because of its ability to produce a drier sludge cake. The pressure filters consist of a series of plates and frames separated by a cloth medium. Sludge is forced into the filter under pressure, while the filtrate is drawn off. When maximum pressure is reached, the influent-sludge flow is stopped and the pressure filter is allowed to discharge the residual filtrate prior to opening the filter and allowing the filter cake to drop by gravity to a conveyor belt below the filter press. The pressure filter operates at a pressure between 689 and 1380 kPa (100 and 200 psig) and takes 1.5 to 4 h for the pressure cycle. Normally, 20 to 30 min is required to remove the filter cake. The sludge cakes will vary from 20 to 25 percent for waste activated sludge to 50 percent for primary sludge. Chemical conditioning is necessary to obtain good dewatering of the sludges.

Belt-Press Filters The newest filter for handling waste activated sludge is the belt-press filter. The belt press utilizes a continuous cloth-filter belt. Waste activated sludge is spread over the filter medium, and water is removed initially by gravity. The open belt with the sludge moves into contact with a second moving belt, which squeezes the sludge layer between rollers with ever-increasing pressure. The sludge cake is removed at the end of the filter press by a knife blade, with the sludge dropping by gravity to a conveyor belt. Belt-press filters can produce sludge with 20–30 percent solids.

Sand Beds Sand filter beds can be used to dewater either anaerobically or aerobically digested sludges. They work best on relatively small treatment systems located in relatively dry areas. The sand bed consists of coarse gravel graded to fine sand in a series of layers to a depth of 0.45 to 0.6 m (1.5 to 2 ft). The digested sludge is placed over the entire filter surface to a depth of 0.3 m (12 in) and allowed to sit until dry. Free water will drain through the sand bed to an open pipe underdrain system and be removed from the filter. Air drying will slowly remove the remaining water. The sludge must be cleaned from the bed by hand prior to adding a second layer of sludge. The sludge layer will drop from an initial thickness of 3 m (12 in) to about 0.006 m (¼ in). An open sand bed can generally handle 49 to 122 kg dry solids/(m^2·year) [10 to 25 lb/(ft^2·year)]. Covered sand beds have been used in wet climates as well as in cold climates, but economics does not favor their use.

SLUDGE DISPOSAL

Incineration Incineration has been used to reduce the volume of sludge after dewatering. The organic fractions in sludges lend themselves to incineration if the sludge does not have an excessive water content. Multiple-hearth and fluid-bed incinerators have been extensively used for sludge combustion.

A multiple-hearth incinerator consists of several hearths in a vertical cylindrical furnace. The dewatered sludge is added to the top hearth and is slowly pushed through the incinerator, dropping by gravity to the next lower layer until it finally reaches the bottom layer. The top layer is used for drying the sludge with the hot gases from the

lower layers. As the temperature of the furnace increases, the organics begin to degrade and undergo combustion. Air is used to add the necessary oxygen and to control the temperature during combustion. It is very important to keep temperatures above 600° C to ensure complete oxidation of the volatile organics. One of the problems with the multiple-hearth incinerator is volatilization of odorous organics during the drying phase before the temperature reaches combustion levels. Even afterburners on the exhaust-gas line may not be adequate for complete oxidation. Air-pollution-control devices are required on all incinerators to remove fly ash and corrosive gases. The ash from the incinerator must be cooled, collected, and conveyed back to the environment, normally to a sanitary landfill for burial. The residual ash will weigh from 10 to 30 percent of the original dry weight of the sludge. Supplemental fuels are needed to start the incinerator and to ensure adequate temperatures with sludges containing excessive moisture, such as activated sludge. Heat recovery from wastes is being given more consideration. It is possible to combine the sludges with other wastes to provide a better fuel for the incinerator.

A fluid-bed incinerator uses hot sand as a heat reservoir for dewatering the sludge and combusting the organics. The turbulence created by the incoming air and the sand suspension requires the effluent gases to be treated in a wet scrubber prior to final discharge. The ash is removed from the scrubber water by a cyclone separator. The scrubber water is normally returned to the treatment process and diluted with the total plant effluent. The ash is normally buried.

Sanitary Landfills Dewatered sludge, either raw or digested, is often buried in a sanitary landfill to minimize the environmental impact. Increased concern over sanitary landfills has made it more difficult simply to bury dewatered sludge. Sanitary landfills must be made secure from leachate and be monitored regularly to ensure that no environmental damage occurs. The moisture content of most sludges makes them a problem at sanitary landfills designed for solid wastes, requiring separate burial even at the same landfill.

Land Spreading The nutrient content of most sludges makes them useful as fertilizers or as soil conditioners if properly mixed with the surface soil. Land spreading has gained in popularity in agricultural areas. Normally, the rate of application of sludge to land is controlled by the nitrogen content of the sludge. Since nitrogen uptake varies with different crops, nitrogen application is limited to approximately twice the annual uptake of nitrogen by the proposed crop. Approximately one-half of the nitrogen is readily available in sludge. Nutrient release with sludge is slower than with chemical fertilizers, allowing the nutrients to become available as the crop needs it. Activated sludge appears to be an excellent soil conditioner because the humus material in the sludge provides a good matrix for root growth, while the nutrient elements are released in approximately the right combination for optimal plant growth. There is a growing concern over heavy metals in some sludge, and care should be taken to minimize heavy-metal concentrations in sludges placed on the land. Since heavy metals cannot be easily removed from sludges, it is important to prevent them from entering the wastewater-treatment system. Greater concern will be placed on other potentially toxic or hazardous materials, including some organic compounds such as pesticides and PCBs. Land spreading of sludge requires careful application of the sludge at the surface and its mixing with the soil. Soil microbes will assist in further stabilization of any biodegradable organics remaining. Land spreading of sludge will become more popular as energy and nutrients become scarcer.

MANAGEMENT OF SOLID WASTES

INTRODUCTION

"Solid wastes" are all the wastes arising from human and animal activities that are normally solid and that are discarded as useless or unwanted. The term as used in this subsection is all-inclusive, and it encompasses the heterogeneous mass of throwaways. The three R's should be applied to Solid Wastes: Reuse, Recycle, and Reduce. When these have been implemented, management of residual solid waste can be addressed.

Functional Elements The activities associated with the management of solid wastes from the point of generation to final disposal have been grouped into the functional elements identified in Fig. 25-59. By considering each fundamental element separately, it is possible to (1) identify the fundamental element and (2) develop, when possible, quantifiable relationships for the purpose of making engineering comparisons, analyses, and evaluations.

Waste Reduction Processes can be redesigned to reduce the amount of waste generated. For example, transfer lines between processes can be blown clear pneumatically to drive liquid into the batch mix tank.

Waste Generation Waste generation encompasses those activities in which materials are identified as no longer being of value and are either thrown away or gathered together for disposal. From the standpoint of economics, the best place to sort waste materials for recovery is at the source of generation.

Reuse Waste may be diverted to reuse. For example, containers may be cleaned and reused or the waste from one process may become the feedstock for another.

On-Site Handling, Storage, and Processing This functional element encompasses those activities associated with the handling, storage, and processing of solid wastes at or near the point of generation. On-site storage is of primary importance because of the aesthetic considerations, public health, public safety, and economics involved.

Collection The functional element of collection includes the gathering of solid wastes and the hauling of wastes after collection to the location where the collection vehicle is emptied. As shown in Fig. 25-59, this location may be a transfer station, a processing station, or a landfill disposal site.

Transfer and Transport The functional element of transfer and transport involves two steps: (1) the transfer of wastes from the smaller collection vehicle to the larger transport equipment and (2) the subsequent transport of the wastes, usually over long distances, to the disposal site.

Processing and Recovery The functional element of processing and recovery includes all the techniques, equipment, and facilities used both to improve the efficiency of the other functional elements and to recover usable materials, conversion products, or energy from solid wastes. Materials that can be recycled are exported to facilities equipped to do so. Residues go to disposal.

Disposal The final functional element in the solid-waste-management system is disposal. Disposal is the ultimate fate of all solid wastes, whether they are wastes collected and transported directly to a landfill site, semisolid wastes (sludge) from industrial treatment plants and air-pollution-control devices, incinerator residue, compost, or other substances from various solid-waste processing plants that are of no further use.

Solid-Waste-Management Systems Practical aspects associated with solid-waste-management systems not covered in the presentation include financing, operations, equipment management, personnel, reporting, cost accounting and budgeting, contract administration, ordinances and guidelines, and public communications.

UNITED STATES LEGISLATION, REGULATIONS, AND GOVERNMENTAL AGENCIES

Much of the current activity in the field of solid-waste management, especially with respect to hazardous wastes and resources recovery, is a direct consequence of legislation. It is imperative to have a working knowledge of waste regulations, including RCRA (for EPA hazardous waste); TSCA (Toxic Substances Control Act) for PCBs and toxic waste; Solid Waste Disposal Act; the Clean Air Act; and PSD (prevention of

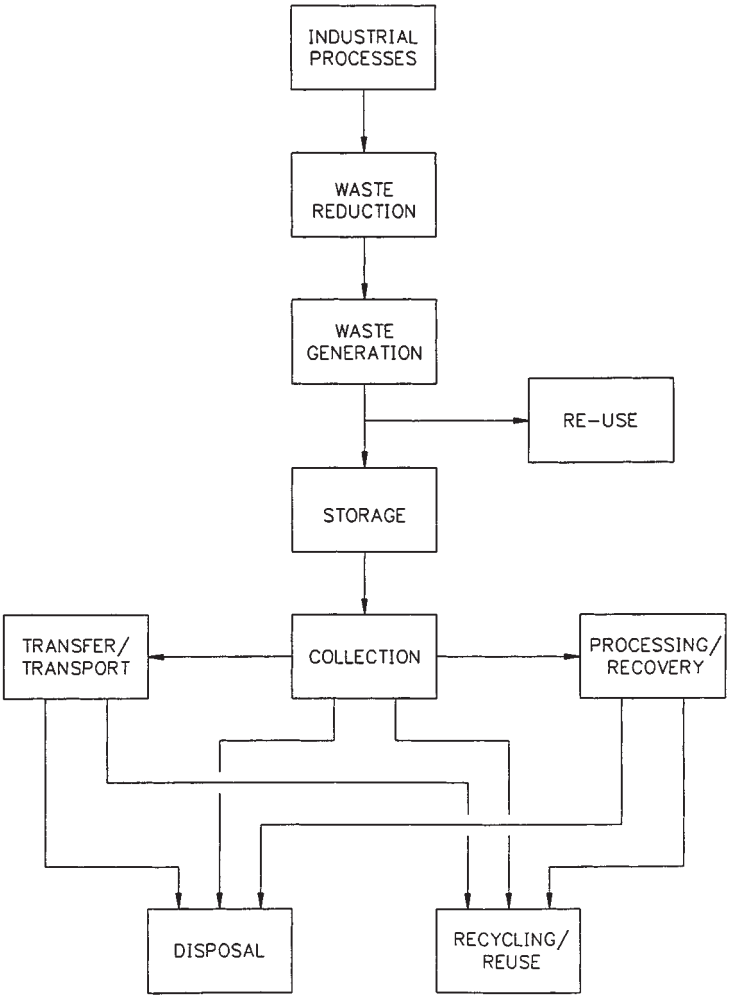


FIG. 25-59 Functional elements in a solid-waste management system. (*Updated from G. Tchobanoglous, H. Theisen, and R. Eliassen,* Solid Wastes: Engineering and Management Issues, *McGraw-Hill, New York, 1977.*)

significant deterioration) regulations. The Clean Air Act has far-reaching implications for any waste-related operation (e.g., incineration or landfill) that emits particulates or gaseous emissions. Primary elements of the act are Title I, dealing with fugitive emissions monitoring, Title III with reduction of organic hazardous air pollutants, and Title V, operating permits. The 1990 amendments have added a significant permitting burden for industrial plants and require additional controls for HAPs (hazardous air pollutants). In addition, state and local regulations apply to waste operations. Regulations are explored in detail in "Introduction to Waste Management" elsewhere in this section.

Regulations have been adopted by federal, state, and local agencies to implement the legislation. Before any design and construction work is undertaken, these regulations must be monitored due to continuous revisions.

GENERATION OF SOLID WASTES

Solid wastes, as noted previously, include all solid or semisolid materials that are no longer considered of sufficient value to be retained in a given setting. The types and sources of solid wastes, the physical and chemical composition of solid wastes, and typical solid-waste generation rates are considered in this subsection.

Types of Solid Wastes The term *solid wastes* is all-inclusive and encompasses all sources, types of classifications, compositions, and properties. As a basis for subsequent discussions, it will be helpful to define the various types of solid wastes that are generated. It is important to note that the definitions of solid-waste terms and the classifications vary greatly in practice and in literature. Consequently, the use of published data requires considerable care, judgment, and common sense. The following definitions are intended to serve as a guide.

1. *Food wastes.* Food wastes are the animal, fruit, or vegetable residues (also called *garbage*) resulting from the handling, preparation, cooking, and eating of foods. The most important characteristic of these wastes is that they are putrescible and will decompose rapidly, especially in warm weather.
2. *Rubbish.* Rubbish consists of combustible and noncombustible solid wastes, excluding food wastes or other putrescible materials. Typically, combustible rubbish consists of materials such as paper, cardboard, plastics, textiles, rubber, leather, wood, furniture, and garden trimmings. Noncombustible rubbish consists of items such as glass, crockery, tin cans, aluminum cans, ferrous and other nonferrous metals, dirt, and construction wastes.
3. *Ashes and residues.* These are the materials remaining from the burning of wood, coal, coke, and other combustible wastes.

Residues from power plants normally are composed of fine, powdery materials, cinders, clinkers, and small amounts of burned and partially burned materials.

4. *Demolition and construction wastes.* Wastes from razed building and other structures are classified as demolition wastes. Wastes from the construction, remodeling, and repair of commercial and industrial buildings and other similar structures are classified as construction wastes. These wastes may include dirt, stones, concrete, bricks, plaster, lumber, shingles, and plumbing, heating, and electrical parts.

5. *Special wastes.* Wastes such as street sweepings, roadside litter, catch-basin debris, dead animals, and abandoned vehicles are classified as special wastes.

6. *Treatment-plant wastes.* The solid and semisolid wastes from water, wastewater, and industrial waste-treatment facilities are included in this classification.

7. *Agricultural wastes.* Wastes and residues resulting from diverse agricultural activities, such as the planting and harvesting of row, field, and tree and vine crops, the production of milk, the production of animals for slaughter, and the operation of feedlots are collectively called agricultural wastes.

Hazardous Wastes The U.S. EPA has defined hazardous waste in RCRA regulations, CFR Parts 260 and 261. A waste may be hazardous if it exhibits one or more of the following characteristics: (1) ignitability, (2) corrosivity, (3) reactivity, and (4) toxicity. A detailed definition of these terms was first published in the *Federal Register* on May 19, 1980, pages 33, 121–122. A waste may be hazardous if listed in Appendix VIII.

In the past, hazardous wastes were often grouped into the following categories: (1) radioactive substances, (2) chemicals, (3) biological wastes, (4) flammable wastes, and (5) explosives. The chemical category included wastes that were corrosive, reactive, and toxic. The principal sources of hazardous biological wastes are hospitals and biological-research facilities.

Sources of Industrial Wastes Knowledge of the sources and types of solid wastes, along with data on the composition and rates of generation, is basic to the design and operation of the functional elements associated with the management of solid wastes.

Conventional Wastes Sources and types of industrial solid wastes generated by Standard Industrial Classification (SIC) group classification are reported in Table 25-49. The expected specific wastes in the table are those that are most readily identifiable.

Hazardous Wastes Hazardous wastes are generated in limited amounts throughout most industrial activities. In terms of generation, concern is with the identification of amounts and types of hazardous wastes developed at each source, with emphasis on those sources where significant waste quantities are generated.

The USEPA released "Biennial RCRA Hazardous Waste Report" in November 1994. The six-volume report, which represents comprehensive data on the generation and management of hazardous waste in the United States during 1991, noted that 306 million tons of hazardous waste generated that year represented an increase of 108 million tons compared with the 198 million tons generated in 1989. The number of large-quantity generators increased by about 3000 from 20,426 reporting in 1989. The number of waste treatment, storage, and disposal (TSD) facilities increased from 3000 to 3862 during the same period. Less than 5 percent—13 million tons—of the 306 million tons generated during 1991 were shipped offsite to commercial TSD facilities.

The majority—76 percent—of the 306 million tons of hazardous waste generated during 1991 was managed in aqueous waste-treatment units. Land disposal accounted for another 9 percent of the total, divided as follows: 23 million tons injected into underground wells; 1.7 million tons sent to landfills; 240,00 tons placed in surface impoundments; and 52,000 tons managed by land farming. Resource-recovery operations managed 2 percent of the 306 million tons, with solvent-recovery units managing 3.6 million tons; fuel-blending units, 1.4 million tons; metals recovery, 1 million tons; and other methods such as acid regeneration and waste oil recovery accounting for 480,000 tons. Thermal treatment systems burned 1.1 percent of the hazardous wastes generated in 1991: 1.9 million tons were incinerated, and 1.5 million tons were used as fuel in boilers and industrial furnaces.

The generation of hazardous wastes by spillage must also be considered. The quantities of hazardous wastes that are involved in spillage usually are not known. After a spill, the wastes requiring collection and disposal are often significantly greater than the amount of spilled wastes, especially when an absorbing material, such as straw, is used to soak up liquid hazardous wastes or when the soil into which a hazardous liquid waste has percolated must be excavated. Both the straw and liquid and the soil and the liquid are classified as hazardous wastes.

Properties of Solid Wastes Information on the properties of solid wastes is important in evaluating alternative equipment needs, systems, and management programs and plans.

Physical Composition Information and data on the physical composition of solid wastes including (1) identification of the individual components that make up industrial and municipal solid wastes, (2) density of solid wastes, and (3) moisture content are presented below.

1. *Individual components.* Components that typically make up most industrial and municipal solid wastes and their relative distribution are reported in Table 25-50. Although any number of components could be selected, those listed in the table have been chosen because they are readily identifiable, are consistent with component categories reported in the literature, and are adequate for the characterization of solid wastes for most applications.

2. *Density.* Typical densities for various wastes as found in containers are reported by source in Table 25-50. Because the densities of solid wastes vary markedly with geographical location, season of the year, and length of time in storage, great care should be used in selecting typical values.

3. *Moisture content.* The moisture content of solid wastes usually is expressed as the mass of moisture per unit mass of wet or dry material. In the wet-mass method of measurement, the moisture in a sample is expressed as a percentage of the wet mass of the material; in the dry-mass method, it is expressed as a percentage of the dry mass of the material. In equation form, the wet-mass moisture content is expressed as follows:

$$\text{Moisture content } (\%) = \left(\frac{a-b}{a}\right) \times 100 \qquad (25\text{-}22)$$

where: a = initial mass of sample as delivered
b = mass of sample after drying

Typical data on the moisture content for the solid-waste components are given in Table 25-51. For most industrial solid wastes, the moisture content will vary from 10 to 25 percent.

Chemical Composition Information on the chemical composition of solid wastes is important in evaluating alternative processing and recovery options. If solid wastes are to be used as fuel, the four most important properties to be known are:

1. Proximate analysis
   a. Moisture (loss at 105° C for 1 h)
   b. Volatile matter (additional loss on heating to 950° C)
   c. Ash (residue after burning)
   d. Fixed carbon (remainder)
2. Fusion point of ash
3. Ultimate analysis, percent of C (carbon), H (hydrogen), O (oxygen), N (nitrogen), S (sulfur), and ash
4. Heating value
5. Organic chlorine

Typical proximate-analysis data for the combustible components of industrial and municipal solid wastes are presented in Table 25-52.

Typical data on the inert residue and energy values for solid wastes may be converted to a dry basis by using Eq. (25-23).

$$\frac{\text{kJ}}{\text{kg (dry basis)}} = \frac{\text{kJ}}{\text{kg (as discarded)}} \left(\frac{100}{100 - \%\ \text{moisture}}\right) \qquad (25\text{-}23)$$

The corresponding equation on an ash-free dry basis is

TABLE 25-49 Sources and Types of Industrial Wastes*

Code	SIC group classification	Waste-generating processes	Expected specific wastes
19	Ordnance and accessories	Manufacturing, assembling	Metals, plastic, rubber, paper, wood, cloth, chemical residues
20	Food and kindred products	Processing, packaging, shipping	Meats, fats, oils, bones, offal, vegetables, fruits, nuts and shells, cereals
22	Textile mill products	Weaving, processing, dyeing, shipping	Cloth and filter residues
23	Apparel and other finished products	Cutting, sewing, sizing, pressing	Cloth, fibers, metals, plastics, rubber
24	Lumber and wood products	Sawmills, millwork plants, wooden containers, miscellaneous wood products, manufacturing	Scrap wood, shavings, sawdust; in some instances, metals, plastics, fibers, glues, sealers, paints, solvents
25a	Furniture, wood	Manufacture of household and office furniture, partitions, office and store fixtures, mattresses	Those listed under Code 24; in addition, cloth and padding residues
25b	Furniture, metal	Manufacture of household and office furniture, lockers, springs, frames	Metals, plastics, resins, glass, wood, rubber, adhesives, cloth, paper
26	Paper and allied products	Paper manufacture, conversion of paper and paperboard, manufacture of paperboard boxes and containers	Paper and fiber residues, chemicals, paper coatings and filters, inks, glues, fasteners
27	Printing and publishing	Newspaper publishing, printing, lithography, engraving, bookbinding	Paper, newsprint, cardboard, metals, chemicals, cloth, inks, glues
28	Chemicals and related products	Manufacture and preparation of inorganic chemicals (ranging form drugs and soaps to paints and varnishes and explosives)	Organic and inorganic chemicals, metals, plastics, rubber, glass, oils, paints, solvents, pigments
29	Petroleum refining and related industries	Manufacture of paving and roofing materials	Asphalt and tars, felts, paper, cloth, fiber
30	Rubber and miscellaneous plastic products	Manufacture of fabricated rubber and plastic products	Scrap rubber and plastics, lampblack, curing compounds, dyes
31	Leather and leather products	Leather tanning and finishing, manufacture of leather belting and packing	Scrap leather, thread, dyes, oils, processing and curing compounds
32	Stone, clay, and glass products	Manufacture of flat glass, fabrication or forming of glass,; manufacture of concrete, gypsum, and plaster products; forming and processing of stone products, abrasives, asbestos, and miscellaneous non-mineral products	Glass, cement, clay, ceramics, gypsum, asbestos, stone, paper, abrasives
33	Primary metal industries	Melting, casting, forging, drawing, rolling, forming, extruding operations	Ferrous and non-ferrous metals scrap, slag, sand, cores, patterns, bonding agents
34	Fabricated metal products	Manufacture of metal cans, hand tools, general hardware, non-electrical heating apparatus, plumbing fixtures, fabricated structural products, wire, farm machinery and equipment, coating and engraving of metal	Metals, ceramics, sand, slag, scale, coatings, solvents, lubricants, pickling liquors
35	Machinery (except electrical)	Manufacture of equipment for construction, elevators, moving stairways, conveyors, industrial trucks, trailers, stackers, machine tools, etc.	Slag, sand, cores, metal scrap, wood, plastics, resins, rubber, cloth, paints, solvents, petroleum products
36	Electrical	Manufacture of electrical equipment, appliances and communication apparatus, machining, drawing, forming, welding, stamping, winding, painting, plating, baking, firing operations	Metal scrap, carbon, glass, exotic metals, rubber, plastics, resins, fibers, cloth residues, PCBs
37	Transportation equipment	Manufacture of motor vehicles, truck and bus bodies, motor-vehicle parts and accessories, aircraft and parts, ship and boat building, repairing motorcycles and bicycles and parts, etc.	Metal scrap, glass, fiber, wood, rubber, plastics, cloth, paints, solvents, petroleum products
38	Professional scientific controlling instruments	Manufacture of engineering, laboratory, and research instruments and associated equipment	Metals, plastics, resins, glass, wood, rubber, fibers, abrasives
39	Miscellaneous manufacturing	Manufacture of jewelry, silverware, plated ware, toys, amusement, sporting and athletic goods, costume novelties, buttons, brooms, brushes, signs, advertising displays	Metals, glass, plastics, resin, leather, rubber, composition, bone, cloth, straw, adhesives, paints, solvents

*From C.L. Mantell (ed.), *Solid Wastes: Origin, Collection, Processing and Disposal,* Wiley-Interscience, New York, 1975. PCBs added to item 36.

$$\frac{\text{kJ}}{\text{kg (ash-free dry basis)}} = \frac{\text{kJ}}{\text{kg (as discarded)}} \times \left(\frac{100}{100 - \%\ \text{ash} - \%\ \text{moisture}} \right) \quad (25\text{-}24)$$

Representative data on the ultimate analysis of typical industrial and municipal-waste components are presented in Table 25-53. If energy values are not available, approximate values can be determined by using Eq. (25-25), known as the modified Dulong formula, and the data in Table 25-53.

$$\frac{\text{kJ}}{\text{kg}} = 337C + 1428\left(H - \frac{1}{8}O\right) + 95S \quad (25\text{-}25)$$

where: C = carbon, percent
H = hydrogen, percent
O = oxygen, percent
S = sulfur, percent

Quantities of Solid Wastes Representative data on the quantities of solid wastes and factors affecting the generation rates are considered briefly in the following paragraphs.

TABLE 25-50 Typical Data on Distribution of Industrial Wastes Generated by Major Industries and Municipalities*

SIC code	Percent by mass									
	Food wastes†	Paper	Wood	Leather	Rubber	Plastics	Metals	Glass	Textiles	Miscellaneous
20 Food and kindred products	15–20	50–60	5–10	0–2	0–2	0–5	5–10	4–10	0–2	5–15
22 Textile mill products	0–2	40–50	0–2	0–2	0–2	3–10	0–2	0–2	20–40	0–5
23 Apparel and other finished products	0–2	40–60	0–2	0–2	0–2	0–2	0–2	0–2	30–50	0–5
24 Lumber and wood products	0–2	10–20	60–80	0–2	0–2	0–2	0–2	0–2	0–2	5–10
25a Furniture, wood	0–2	20–30	30–50	0–2	0–2	0–2	0–2	0–2	0–5	0–5
25b Furniture, metal	0–2	20–40	10–20	0–2	0–2	0–2	20–40	0–2	0–5	0–10
26 Paper and allied products	0–2	40–60	10–15	0–2	0–2	0–2	5–15	0–2	0–2	10–20
27 Printing and publishing	0–2	60–90	5–10	0–2	0–2	0–2	0–2	0–2	0–2	0–5
28 Chemicals and related products	0–2	40–60	2–10	0–2	0–2	5–15	5–10	0–5	0–2	15–25
29 Petroleum refining and related industries	0–2	60–80	5–15	0–2	0–2	10–20	2–10	0–12	0–2	2–10
30 Rubber and miscellaneous plastic products	0–2	40–60	2–10	0–2	5–20	10–20	0–2	0–2	0–2	0–5
31 Leather and leather products	0–2	5–10	5–10	40–60	0–2	0–2	10–20	0–2	0–2	0–5
32 Stone, clay, and glass products	0–2	20–40	2–10	0–2	0–2	0–2	5–10	10–20	0–2	30–50
33 Primary metal industries	0–2	30–50	5–15	0–2	0–2	2–10	2–10	0–5	0–2	20–40
34 Fabricated metal products	0–2	30–50	5–15	0–2	0–2	0–2	15–30	0–2	0–2	5–15
35 Machinery (except electrical)	0–2	30–50	5–15	0–2	0–2	1–5	15–30	0–2	0–2	0–5
36 Electrical	0–2	60–80	5–15	0–2	0–2	2–5	2–5	0–2	0–2	0–5
37 Transportation equipment	0–2	40–60	5–15	0–2	0–2	2–5	0–2	0–2	0–2	15–30
38 Professional scientific controlling instruments	0–2	30–50	2–10	0–2	0–2	5–10	5–15	0–2	0–2	0–5
39 Miscellaneous manufacturing	0–2	40–60	10–20	0–2	0–2	5–15	2–10	0–2	0–2	5–15
Municipal	10–20	40–60	1–4	0–2	0–2	2–10	3–15	4–16	0–4	5–30

*Adapted in part from D. G. Wilson (ed.), *Handbook of Solid Waste Management,* van Nostrand Reinhold, New York, 1977.
†With the exception of food and kindred products, food wastes are from company cafeterias, canteens, etc.

Typical Generation Rates Typical unit waste-generation rates for selected industrial sources are reported in Table 25-54. Because waste-generation practices are changing so rapidly, the presentation of "typical" waste-generation data may not be reliable.

Factors That Affect Generation Rates Factors that influence the quantity of industrial wastes generated include (1) the extent of salvage and recycle operations, (2) company attitudes, and (3) legislation. The existence of salvage and recycling operations within an industry definitely affects the quantities of wastes collected. Whether such operations affect the quantities generated is another matter. The section entitled "Pollution Prevention" by Louis Theodore points out activities by industrial plants as a result of the 1990 Pollution Prevention Act. Significant reductions in the quantities of solid wastes that are generated will occur when and if companies are willing to change—on their own volition—to conserve national resources, handle waste at its source rather than "end of pipe" pollution control, and to reduce the economic burdens associated with the management of solid wastes. Perhaps the most important factor affecting the generation of certain types of wastes is the existence of local, state, and federal regulations concerning the use and disposal of specific material. In general, the more regulated the waste, the higher the cost for treatment and disposal and the greater the incentive to reduce generation of the waste.

ON-SITE HANDLING, STORAGE, AND PROCESSING

The handling, storage, and processing of solid wastes at the source before they are collected is the second of the six functional elements in the solid-waste-management system.

On-Site Handling On-site handling refers to the activities associated with the handling of solid wastes until they are placed in the containers used for storage before collection. Depending on the type of collection service, handling may also be required to move loaded containers to the collection point and to return the empty containers to the point where they are stored between collections.

Conventional Solid Wastes In most office, commercial, and industrial buildings, solid wastes that accumulate in individual offices or work locations usually are collected in relatively large containers mounted on casters. Once filled, these containers are removed by means of the service elevator, if there is one, and emptied into (1) large storage containers, (2) compactors used in conjunction with the storage containers, (3) stationary compactors that can compress the

TABLE 25-51 Typical Density and Moisture-Content Data for Domestic, Commercial, and Industrial Solid Waste

Item	Density, kg/m³		Moisture content, % by mass	
	Range	Typical	Range	Typical
Residential (Uncompacted)				
Food wastes (mixed)	130–480	290	50–80	70
Paper	40–130	85	4–10	6
Cardboard	40–80	50	4–8	6
Plastics	40–130	65	1–4	2
Textiles	40–100	65	6–15	10
Rubber	100–200	130	1–4	2
Leather	100–260	160	8–12	10
Garden trimmings	60–225	100	30–80	60
Wood	130–320	240	15–40	20
Glass	160–480	195	1–4	2
Tin cans	50–160	90	2–4	3
Nonferrous metals	65–240	160	2–4	2
Ferrous metals	130–1150	320	2–4	2
Dirt, ashes, etc.	320–1000	480	6–12	8
Ashes	650–830	745	6–12	6
Rubbish (mixed)	90–180	130	5–20	15
Residential (compacted)				
In compactor truck	180–450	300	15–40	20
In landfill (normally compacted)	360–500	450	15–40	30*
In landfill (well-compacted)	590–740	600	15–40	30*
Commercial				
Food wastes (wet)	475–950	535	50–85	75
Appliances	150–200	180	0–5	
Wooden crates	110–160	110	10–30	20
Tree trimmings	100–180	150	20–80	50
Rubbish (combustible)	50–180	120	5–25	15
Rubbish (non-combustible)	180–360	300	5–15	10
Rubbish (mixed)	140–180	160	5–20	12
Construction; demolition				
Mixed demolition (non-combustible)	1000–1600	1420	2–10	4
Mixed demolition (combustible)	300–400	360	4–15	8
Mixed construction (combustible)	180–360	260	4–15	8
Broken concrete	1200–1800	1540	0–5	
Industrial wastes				
Chemical sludges (wet)	800–1100	1000	75–99	80
Fly ash	700–900	800	2–10	4
Leather scraps	100–250	160	6–15	10
Metal scraps (heavy)	1500–2000	1780	0–5	
Metal scrap (light)	500–900	740	0–5	
Metal scrap (mixed)	700–1500	900	0–5	
Oils, tars, asphalt	800–1000	950	0–5	2
Sawdust	100–350	290	10–40	15
Textile wastes	100–220	180	6–15	10
Wood (mixed)	400–675	500	10–40	20
Agricultural wastes				
Agricultural (mixed)	400–750	560	40–80	50
Fruit wastes (mixed)	250–750	360	60–90	75
Manure (wet)	900–1050	1000	75–96	94
Vegetable wastes (mixed)	200–700	360	50–80	65

*Depends on degree of surface-water infiltration.

material into bales or into specially designed containers, or (4) other processing equipment.

Hazardous Wastes When hazardous wastes are generated, special containers are usually provided, and trained personnel (OSHA 1910.120 required such workers to have HAZWOPER training) are responsible (or should be) for the handling of these wastes. Hazardous wastes include solids, sludges, and liquids; hence, container requirements vary with the form of waste.

On-Site Storage Factors that must be considered in the on-site storage of solid wastes include (1) the type of container to be used, (2) the container location, (3) public health and aesthetics, (4) the collection methods to be used, and (5) future transport method.

Containers To a large extent, the types and capacities of the containers used depend on the characteristics of the solid wastes to be collected, the collection frequency, and the space available for the placement of containers.

1. *Containers for conventional wastes.* The types and capacities of containers now commonly used for on-site storage of solid wastes are summarized in Table 25-55. The small containers are used in individual offices and work stations. The medium-size and large containers are used at locations where large volumes are generated.

2. *Containers for hazardous wastes.* On-site storage practices are a function of the types and amounts of hazardous wastes generated and the time period over which waste generation occurs. Usually, when large quantities are generated, special facilities that have sufficient capacity to hold wastes accumulated over a period of several days are used. When only small amounts of hazardous wastes are generated on an intermittent basis, they may be containerized, and limited quantities may be stored for periods covering months or years. General information on the storage containers used for hazardous wastes and the conditions of their use is presented in Table 25-56.

Container Location. The location of containers at existing commercial and industrial facilities depends on both the location of available space and service-access conditions. In newer facilities, specific service areas have been included for this purpose. Often, because the containers are not owned by the commercial or industrial activity, the

TABLE 25-52 Typical Proximate-Analysis and Energy-Content Data for Components in Domestic, Commercial, and Industrial Solid Waste*

Component	Proximate analysis, % by mass				Energy content, kJ/kg		
	Moisture	Volatile matter	Fixed carbon	Non-combustible	As collected	Dry	Moisture- and ash-free
Food and food products							
Fats	2.0	95.3	2.5	0.2	37,530	38,296	38,374
Food wastes (mixed)	70.0	21.4	3.6	5.0	4,175	13,917	16,700
Fruit wastes	78.7	16.6	4.0	0.7	3,970	18,638	19,271
Meat wastes	38.8	56.4	1.8	3.1	17,730	28,970	30,516
Paper products							
Cardboard	5.2	77.5	12.3	5.0	16,380	17,278	18,240
Magazines	4.1	66.4	7.0	22.5	12,220	12,742	16,648
Newsprint	6.0	81.1	11.5	1.4	18,550	19,734	20,032
Paper (mixed)	10.2	75.9	8.4	5.4	15,815	17,611	18,738
Waxed cartons	3.4	90.9	4.5	1.2	26,345	27,272	27,615
Plastics							
Plastics (mixed)	0.2	95.8	2.0	2.0	32,000	32,064	32,720
Polyethylene	0.2	98.5	<0.1	1.2	43,465	43,552	44,082
Polystyrene	0.2	98.7	0.7	0.5	38,190	38,266	38,216
Polyurethane	0.2	87.1	8.3	4.4	26,060	26,112	27,316
Polyvinyl chloride	0.2	86.9	10.8	2.1	22,690	22,735	23,224
Wood, trees, etc.							
Garden trimmings	60.0	30	9.5	0.5	6,050	15,125	15,316
Green wood	50.0	42.3	7.3	0.4	4,885	9,770	9,848
Hardwood	12.0	75.1	12.4	0.5	17,100	19,432	19,542
Wood (mixed)	20.0	67.9	11.3	0.8	15,444	19,344	19,500
Leather, rubber, textiles, etc.							
Leather (mixed)	10	68.5	12.5	9.0	18,515	20,572	22,858
Rubber (mixed)	1.2	83.9	4.9	9.9	25,330	25,638	28,493
Textiles (mixed)	10	66.0	17.5	6.5	17,445	19,383	20,892
Glass, metals, etc.							
Glass and mineral	2	—	—	96–99+	196†	200	200
Metal, tin cans	5	—	—	94–99+	1,425†	1,500	1,500
Metals, ferrous	2	—	—	96–99+	—	—	—
Metals, nonferrous	2	—	—	94–99+	—	—	—
Miscellaneous							
Office sweepings	3.2	20.5	6.3	70	8,535	8,817	31,847
Multiple wastes	20 (15–40)	53 (30–60)	7 (5–15)	20 (9–30)	10,470	13,090	17,450
Industrial wastes	15 (10–30)	58 (30–60)	7 (5–15)	20 (10–30)	11,630	13,682	17,892

*Adapted in part from D. G. Wilson (ed.), *Handbook of Solid Waste Management,* Van Nostrand Reinhold, New York, 1977, and G. Tchobanoglous, H. Theisen, and R. Eliassen, *Solid Wastes: Engineering Principles and Management Issues,* McGraw-Hill, New York, 1977.
†Energy content is from coatings, labels, and attached materials.

locations and types of containers to be used for on-site storage must be worked out jointly between the industry and the public or private collection agency.

On-Site Processing of Solid Wastes On-site-processing methods are used to (1) recover usable materials from solid wastes, (2) reduce the volume, or (3) alter the physical form. The most common on-site-processing operations as applied to large commercial and industrial sources include manual sorting, compaction, and incineration. These and other processing operations are considered in the portion of this section dealing with processing and resource recovery. Factors that should be considered in the selection of on-site-processing equipment are summarized in Table 25-57.

COLLECTION OF SOLID WASTES

Information on collection, one of the most costly functional elements, is presented in four parts dealing with (1) the types of collection services, (2) the types of collection systems, (3) an analysis of collection systems, and (4) the general methodology involved in setting up collection routes.

Collection Services The various types of collection services now used for commercial-industrial sources are described in this subsection.

Commercial-Industrial The collection service provided to large commercial and industrial activities typically is centered in the use of large moveable and stationary containers and large stationary compactors. Compactors are of the type that can be used to compress material directly into large containers (see Fig. 25-60) or to form bales that are then placed in large containers.

Hazardous Wastes Hazardous Wastes for delivery to a treatment or disposal facility normally are collected by the waste producer or a licensed, specialized hauler. Typically, the loading of collection vehicles is completed in one of two ways: (1) wastes stored in large-capacity tanks are either drained or pumped into collection vehicles, and (2) wastes stored in sealed drums or other sealed containers are loaded by hand or by mechanical equipment onto flatbed trucks. To avoid accidents and possible loss of life, two collectors should always be assigned when hazardous wastes are to be collected.

Types of Collection Systems On the basis of their mode of operation, collection systems are classified into two categories: (1) hauled-container systems and (2) stationary-container systems.

Hauled-Container Systems (HCS) Collection systems in which the containers used for storage of wastes are hauled to the processing, transfer, or disposal site, emptied, and returned to either their original location or some other location are defined as "hauled-container systems." In most hauled-container systems, a single collector is used. The collector is responsible for driving the vehicle, loading full containers and unloading empty containers, and emptying the contents of the container at the disposal site. In some cases, for safety reasons, both a driver and helper are used.

There are three main types of hauled-container systems: (1) hoist

TABLE 25-53 Typical Ultimate-Analysis Data for Components in Domestic, Commercial and Industrial Solid Waste*

Components	Percent by mass (dry basis)					
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
Foods and food products						
Fats	73.0	11.5	14.8	0.4	0.1	0.2
Food wastes (mixed)	48.0	6.4	37.6	2.6	0.4	5.0
Fruit wastes	48.5	6.2	39.5	1.4	0.2	4.2
Meat wastes	59.6	9.4	24.7	1.2	0.2	4.9
Paper products	45.4	6.1	42.1	0.3	0.1	6.0
Cardboard	43.0	5.9	44.8	0.3	0.2	5.0
Magazines	32.9	5.0	38.6	0.1	0.1	23.3
Newsprint	49.1	6.1	43.0	<0.1	0.2	23.3
Paper (mixed)	43.4	5.8	44.3	0.3	0.2	6.0
Waxed cartons	59.2	9.3	30.1	0.1	0.1	1.2
Plastics						
Plastics (mixed)	60.0	7.2	22.8	—	—	10.0
Polyethylene	85.2	14.2	—	<0.1	<0.1	0.4
Polystyrene	87.1	8.4	4.0	0.2	—	0.3
Polyurethane†	63.3	6.3	17.6	6.0	<0.1	4.3
Polyvinyl chloride†	45.2	5.6	1.6	0.1	0.1	2.0
Wood, trees, etc.						
Garden trimmings	46.0	6.0	38.0	3.4	0.3	6.3
Green timber	50.1	6.4	42.3	0.1	0.1	1.0
Hardwood	49.6	6.1	43.2	0.1	<0.1	0.9
Wood (mixed)	49.5	6.0	42.7	0.2	<0.1	1.5
Wood chips (mixed)	48.1	5.8	45.5	0.1	<0.1	0.4
Glass, metals, etc.						
Glass and mineral‡	0.5	0.1	0.4	<0.1	—	98.9
Metals (mixed)	4.5	0.6	4.3	<0.1	—	90.5
Leather, rubber, textiles						
Leather (mixed)	60.0	8.0	11.6	10.0	0.4	10.0
Rubber (mixed)	69.7	8.7	—	—	1.6	20.0
Textiles (mixed)	48.0	6.4	40.0	2.2	0.2	3.2
Miscellaneous						
Office sweepings	24.3	3.0	4.0	0.5	0.2	68.0
Oils, paints	66.9	9.6	5.2	2.0	—	16.3
Refuse-derived fuel (RAF)	44.7	6.2	38.4	0.7	<0.1	9.9

*Adapted in part from D. G. Wilson (ed.), *Handbook of Solid Waste Management,* Van Nostrand Reinhold, New York, 1977, and G. Tchobanoglous, H. Theisen, and R. Eliassen, *Solid Wastes: Engineering Principles and Management Issues,* McGraw-Hill, New York, 1977.
†Remainder is chlorine.
‡Organic content is from coatings, labels, and other attached materials.

truck, (2) tilt-frame container, and (3) tractor trailer. Typical data on the containers and collection vehicles used with these systems are reported in Tables 25-58 and 25-59, respectively.

1. *Container carrier systems.* Container carrier systems are being used in a limited number of cases, the most important of which are (1) the collection of wastes from only a few pickup points at which a considerable amount of waste is generated and (2) the collection of bulky items and industrial rubbish not suitable for collection with compaction vehicles, and (3) small, heavy loads such as scrap metal.

2. *Roll-off container systems.* Systems that use tilt-frame-loaded vehicles and large containers, often called "roll-off boxes," are ideally suited for the collection of all typed of solid waste and rubbish from locations where the generation rate warrants the use of large containers. Open-top containers are used routinely at warehouses and construction sites. Large containers used in conjunction with stationary compactors are common at commercial and industrial services and transfer stations. Because of the large volume that can be hauled, the use of tilt-frame hauled-container systems has become widespread, especially among private collectors servicing industrial accounts. Roll-off boxes now predominate; however, permanently-attached, open-top, self-dumping containers are still in use. Self-contained compactors of 14–30 m^3 capacity are used in conjunction with hoist trucks. This type has an integral ram and cylinder permanently built into the roll-off container. Other compactors are of the external type, with a detachable roll-off container. Compactors are excellent for volume reduction of bulky material such as cardboard boxes. In many areas, cardboard-recycling facilities will provide the compacting equipment, and the generator experiences a reduction in waste disposal costs.

3. *Tractor-trailer systems.* The application of tractor trailers is similar to that for tilt-frame-container systems. The use of a separate tractor increases the number of axles and the net weight of waste that can be hauled. Tractor trailers are better for the collection of especially heavy rubbish, such as sand, timber, and metal scrap, and they are often are used for the collection of demolition wastes at construction sites.

Stationary-Container Systems (SCS) Collection systems in which the containers used for the storage of wastes remain at the point of waste generation, except for occasional short trips to the collection vehicle, are defined as stationary-container systems. Labor requirements for mechanically loaded stationary-container systems are essentially the same as for hauled-container systems. There are two main types of stationary-container systems: (1) those in which self-loading compactors are used and (2) those in which manually loaded vehicles are used.

1. *Systems with self-loading compactors.* Container size and utilization are not as critical in stationary-container systems using self-loading collection vehicles equipped with a compaction mechanism (see Fig. 25-61 and Table 25-59) as they are in hauled-container systems. Trips to the disposal site, transfer station, or processing station are made after the contents of a number of containers have been collected and compacted and the collection vehicle is full. Because a variety of container sizes and types are available, these systems may be used for the collection of all types of wastes. Container sizes vary from relatively small sizes (0.6 m^3) to sizes comparable to those handled with a hoist truck (see Table 25-58).

2. *Systems with manually loaded vehicles.* The major application of manual transfer and loading methods is in the collection of res-

TABLE 25-54 Unit Solid-Waste-Generation Rates for Selected Industrial Sources

Source	Unit	Range
Canned and frozen foods	Metric tons/metric tons of raw product	0.04–0.06
Printing and publishing	Metric tons/metric tons of raw paper	0.08–0.10
Automotive	Metric tons/vehicle produced	0.6–0.8
Petroleum refining	Metric tons/(employee day)	0.04–0.05
Rubber	Metric tons/metric tons of raw rubber	0.01–0.3

TABLE 25-55 Data on the Types and Sizes of Containers Used for On-Site Storage of Solid Wastes

	Capacity			Dimensions*	
Container type	Unit	Range	Typical	Unit	Typical
Small capacity					
Plastic or metal (office type)	L	16–40	28	mm	(180 × 300) B × (260 × 380) T × 380 H
Plastic or galvanized metal	L	75–150	120	mm	510 D × 660 H
Barrel, plastic, aluminum, or fiber barrel	L	20–250	120	mm	510 D × 660 H
Disposable paper bags (standard, leak-resistant, and leakproof)	L	75–210	120	mm	380 W × 300 d × 1100 H
Disposable plastic bag	L	20–200	170	mm	460 W × 380 d × 1000 H
Medium capacity					
Side or top loading	m^3	0.75–9	3	mm	1830 W × 1070 d × 1650 H
Bulk bags	m^3	0.3–2	1	mm	1000 W × 1000 d × 1000 H
Large capacity					
Open-top, roll-off (also called debris boxes)	m^3	9–38	27	mm	2440 W × 1830 H × 6100 L
Used with stationary compactor	m^3	15–30	23	mm	2440 W × 1830 H × 5490 L
Equipped with self-contained compaction mechanism	m^3	15–30	23	mm	2440 W × 2440 H × 6710 L
Trailer-mounted					
Open-top	m^3	15–38	27	mm	2440 W × 3660 H × 6100 L
Enclosed, equipped with self-contained compaction mechanism	m^3	15–30	27	mm	2440 W × 3660 H × 7320 L

*B = bottom, T = top, D = diameter, H = height, L = length, W = width, and d = depth.

TABLE 25-56 Typical Data on Containers Used for Storage and Transport of Hazardous Wastes

	Container		
Waste category	Type	Capacity	Auxiliary equipment and conditions of use
Radioactive substances	Lead encased in concrete	Varies with waste	Isolated storage buildings; high-capacity hoists and lighting equipment; special container markings
	Lined metal drums	210 L	
Corrosive, reactive, and toxic chemicals	Metal drums	210 L	Washing facilities for empty containers; special blending precautions to prevent hazardous reactions; incompatible wastes stored separately
	Plastic drums	210 L, up to 500 L	
	Lined metal drums	210 L	
	Lined and unlined storage tanks	Up to 20 m^3	
Liquids and sludges	Drums	142–3,400 L	Drum hand-trucks, pallets, forklifts
	Trucks	11–30 m^3	Transfer piping, hoses, pumps
	Vacuum tankers	11–15 m^3	Transfer piping, hoses, pumps
Biological wastes	Sealed plastic bags	120 L	Heat sterilization prior to bagging; special heavy-duty bags with hazard warning printed on sides
	Lined boxes, Lined metal drums	57 L	
Flammable wastes	Metal drums	210 L	Fume ventilation; temperature control
	Storage tanks	Up to 20 m^3	
Explosives	Shock-absorbing containers	Varies	Temperature control; special container markings

idential wastes and litter. For industrial and hazardous waste, manual loading is the exception, not the rule. It is used for the collection of industrial wastes when pickup points are inaccessible to the collection vehicle.

Equipment for Hazardous-Wastes Collection The equipment used for collection varies with the characteristics of the wastes. For short-haul distances, drum storage and collection with an enclosed trailer are often preferred methods. Full-size drums are usually shipped four to a pallet. Smaller sizes are stacked and/or wrapped up to 10 per pallet. As hauling distances increase, larger tank trucks, trailers, and railroad tank cars are used.

Equipment for Superfund Waste Shipment RCRA hazardous waste that has been spilled, improperly landfilled, or dredged from defunct lagoons is a CERCLA waste, more commonly referred to as a Superfund waste. For clean-ups where offsite treatment is the chosen solution, soil is excavated and placed in 15-m^3 roll-off box or dump body truck. The trucks may be lined with polyethylene to reduce decontamination and eliminate sticking of the load to the steel body during freezing weather. The waste is shipped to a landfill, incinerator, or other treatment facility. If the waste is a sludge (as found in a lagoon), dewatering to 50 percent solids is normally performed on site via plate and frame filter press. This may be followed by mixing with bulking reagents to eliminate free water. The alternative is shipping the waste in a tanker or other container that retains free liquid.

Occasionally, a small clean-up of a few tons may occur. These are usually handled via placing the waste in open-topped drums that are sealed with a lid and ring closure. Consultation with the ultimate treatment facility is important to select the correct drum size and material and eliminate the need for repackaging the waste.

Transportation Costs Most waste trucking is done by commercial and hazardous waste firms. Costs are quoted per load, based on cost for transport (charged per load mile) from point of generation to its destination at a landfill or TSD facility. A strategy which permits shipment of full truckloads minimizes the transportation cost per ton.

TABLE 25-57 Factors That Should Be Considered in Evaluating On-Site Processing Equipment

Factor	Evaluation
Capabilities	What will the device or mechanism do? Will its use be an improvement over conventional practices?
Reliability	Will the equipment perform its designated functions with little attention beyond preventive maintenance? Has the effectiveness of the equipment been demonstrated in use over a reasonable period of time or merely predicted?
Service	Will servicing capabilities beyond those of the local building maintenance staff be required occasionally? Are properly trained service personnel available through the equipment manufacturer or the local distributor?
Safety of operation	Is the proposed equipment reasonably foolproof so that it may be operated by tenants or building personnel with limited mechanical knowledge or abilities? Does it have adequate safeguards to discourage careless use?
Ease of operation	Is the equipment easy to operate by a tenant or by building personnel? Unless functions and actual operations of equipment can be carried out easily, they may be ignored or bypassed by paid personnel and most often by "paying" tenants.
Efficiency	Does the equipment perform efficiently and with a minimum of attention? Under most conditions, equipment that completes an operational cycle each time that it is used should be selected.
Environmental effects	Does the equipment pollute or contaminate the environment? When possible, equipment should reduce environmental pollution presently associated with conventional functions.
Health hazards	Does the device, mechanism, or equipment create or amplify health hazards?
Aesthetics	Do the equipment and its arrangement offend the senses? Every effort should be made to reduce or eliminate offending sights, odors, and noises.
Economics	What are the economics involved? Both first and annual costs must be considered. Future operation and maintenance costs must be assessed carefully. All factors being equal, equipment produced by well-established companies, having a proven history of satisfactory operation, should be given appropriate consideration.
Flexibility	Will the equipment or its placement allow future changes to the process to handle wastes with differing characteristics?

*From G. Tchobanoglous, H. Theisen, and R. Eliassen, *Solid Wastes: Engineering Principles and Management Issues,* McGraw-Hill, New York, 1977.

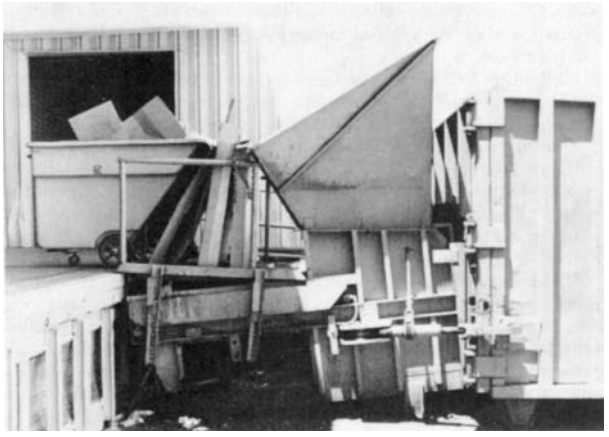


FIG. 25-60 Small compactor used in conjunction with a detachable roll-off container. Note the wheeled container used to collect wastes within the warehouse.

TRANSFER AND TRANSPORT

The functional element of transfer and transport refers to the means, facilities, and appurtenances used to effect the transfer of wastes from relatively small collection vehicles to larger vehicles and to transport them over extended distances to either processing centers or disposal sites. Transfer and transport operations become a necessity when haul distances to available disposal sites or processing centers increase to a point at which direct hauling is no longer economically feasible.

Transfer Stations Important factors that must be considered in the design of transfer stations include (1) the type of transfer operation to be used, (2) capacity requirements, (3) equipment and accessory requirements, and (4) environmental requirements.

Types of Transfer Stations Depending on the method used to load the transport vehicles, transfer stations may be classified into three types: (1) direct-discharge, (2) storage-discharge, and (3) combined direct- and storage-discharge.

1. *Direct discharge.* In a direct-discharge transfer station, wastes from the collection vehicles are usually emptied directly into the vehicle to be used to transport them to a place of final disposition. To accomplish this, these transfer stations are usually constructed in a two-level arrangement. Either the unloading dock or platform from which wastes from collection vehicles are discharged into the transport trailers is elevated, or the transport trailers are located in a depressed ramp (see Fig. 25-62). Direct-discharge transfer stations employing stationary compactors also are popular.

TABLE 25-58 Typical Data on Container Capacities for Use with Various Collection Systems for Solid Waste

Collection		Typical range of container capacities,* m^3
Vehicle	Container type	
Hauled-container systems		
Hoist-truck	Open and covered, also used with stationary compactor	2–9
Tilt-frame/roll-off container	Open-top, roll-off containers	8–40
	Can be used in conjunction with stationary compactor	10–30
	Equipped with self-contained compaction mechanism	15–30
Tractor trailer	Open-top trash trailers	10–30
	Enclosed trailer-mounted containers equipped with self-contained compaction mechanism	15–30
Stationary-container systems	Long-body dump trailer	15–30
Compactor, mechanically loaded	Open-top and enclosed top- and front- or rear-loading	0.6–6
Compactor, manually loaded	Small plastic or galvanized metal containers, disposable paper and plastic bags	75–200 L†

*See Table 25-55 for typical dimensions.
†Loaded mass of container should not exceed 30 kg.

TABLE 25-59 Typical Data on Vehicles Used for Collection of Solid Wastes

Collection vehicle			Typical overall collection-vehicle dimensions				
Type	Available container or truck body capacities,* m^3	Number of axles	With indicated container or truck body capacity,* m^3	Width, mm	Height, mm	Length,* mm	Unloading method
Hauled-container systems							
Hoist-truck	2–9	2	7.6	2440	2030–2540	2800–3800	Gravity, bottom-opening
Tilt-frame	8–40	3	22.9	2440	2030–2290	5590–7620	Gravity, inclined-tipping
Truck-tractor trash trailer	10–30	3	30.6	2440	2290–3800	5590–11,430	Gravity, inclined-tipping
Roll-off container	8–30	3–4	37	2440	12400–2700	9100–10,000	Gravity, inclined tipping
Stationary-container systems							
Compactor (mechanically loaded)							
Front-loading	15–35	3	22.9	2440	3560–3800	6100–7370	Hydraulic ejector panel
Side-loading	6–28	3	22.9	2440	3350–3000	5590–6600	Hydraulic ejector panel
Rear-loading	6–24	2	15.3	2440	3175–3430	5330–5824	Hydraulic ejector panel
Compactor (manually loaded)							
Side-loading	6–28	3	28.3	2440	3350–3800	6100–7620	Hydraulic ejector panel
Rear-loading	6–24	2	15.3	2440	3175–3430	5330–5840	Hydraulic ejector panel

*From front of truck to rear of container or truck body.

2. *Storage discharge.* In the storage-discharge transfer station, wastes are emptied either into a storage pit or onto a platform from which they are loaded into transport vehicles by various types of auxiliary equipment. In a storage-discharge transfer station, storage volume varies from about one-half to 2 days' volume of wastes.

3. *Combined direct and storage discharge.* In some transfer stations, both direct-discharge and storage-discharge methods are used. Usually, these are multipurpose facilities designed to service a broader range of users than a single-purpose facility. In addition to serving a broader range of users, a multipurpose transfer station may house a materials-salvage operation recovery facility.

Capacity Requirements The operating capacity of a transfer station must be such that collection vehicles do not have to wait long to unload. In most cases, it will not be cost-effective to design the station to handle the ultimate peak number of hourly loads. An economic trade-off analysis should be made between the annual cost for the time spent by the collection vehicles waiting to unload against the incremental annual cost of a larger transfer station and/or the use of more transport equipment. Because of the increased cost of transport equipment, a trade-off analysis must also be made between the capacity of the transfer station and the cost of the transport operation, including both equipment and labor components.

Equipment and Accessory Requirements The types and amounts of equipment required vary with the capacity of the station and its function in the waste-management system. Specifically, truck scales should be provided at all medium-size and large transfer stations, both to monitor the operation and to develop meaningful management and engineering data.

Environmental Requirements Most large modern transfer stations are enclosed and are constructed of materials that can be maintained and cleaned easily. For direct-discharge transfer stations with open loading areas, special attention must be given to the problem of blowing papers. Windscreens or other barriers are commonly used. Regardless of type, the station should be designed and constructed so that all accessible areas where rubbish or paper can accumulate are eliminated.

Transfer Means and Methods Motor vehicles, railroads, and barges are the principal means used to transport solid wastes. Pneumatic and hydraulic systems have also been used.

Motor-Vehicle Transport Motor vehicles used to transport solid wastes on highways should satisfy the following requirements: (1) Wastes must be transported at minimum cost. (2) Wastes must be covered during the haul operation. (3) Vehicles must be designed for highway traffic. (4) Vehicle capacity must be such that allowable weight limits are not exceeded. (5) Methods used for unloading must be simple and dependable. The maximum volume that can be hauled in highway transport vehicles depends on the regulations in force in the state in which these vehicles are operated.

1. *Trailers and semitrailers.* In recent years, because of their simplicity and dependability, open-top trailers and semitrailers have found wide acceptance (see Table 25-60). Some trailers are equipped with sumps to collect any liquids that accumulate from the solid wastes. The sumps are equipped with drains so that they can be emptied at the disposal site.



FIG. 25-61 Typical front-loading compactor used in a stationary-container collection system.



FIG. 25-62 Direct-discharge transfer station with open-top trailers located in a depressed ramp under the loading hoppers.

TABLE 25-60 Typical Data on Haul Vehicles Used at Transfer Stations

Type	Capacity per trailer		Dimensions of single trailer			Length of tractor and trailer units, m
	m^3	Metric tons	Width, m	Length, m	Approximate height, empty, m	
Tractor-tandem-trailer	54	11.4	2.44	8.25	4.12	19.8
Tractor-trailer	54	10.0	2.44	8.50	4.12	12.0
	74	17.3	2.44	12.2	4.12	16.0
Tractor-compactor-trailer	58	18.0	2.44	10.2	4.12	14.0

Methods used to unload the transport trailers may be classified as (1) self-emptying and (2) requiring the aid of auxiliary equipment. Self-emptying transport trailers are equipped with mechanisms such as pusher rams, dump body, and moving floors that are part of the vehicle. An advantage of the moving-floor trailer is the rapid turnaround time (typically 6 to 10 min) achieved at the disposal site without the need for auxiliary equipment. Unloading systems that require auxiliary equipment are usually of the pull-off type, in which the wastes are pulled out of the truck by either a moveable bulkhead or wire-cable slings placed forward of the load. Walking floor trailers are self-unloading.

Another auxiliary unloading system that has proven to be very effective and efficient involves the use of moveable, hydraulically operated truck dumps located at the disposal site. Operationally, the trailer is backed up onto one of the tipping ramps, with or without its tractor. The back of the trailer is opened, and the unit is then tilted upward until the wastes fall out by gravity. The time required for the entire unloading operation typically is about 5 min per trip.

2. *Compactors.* Large-capacity containers and container-trailers are used in conjunction with stationary compactors at transfer stations. In some cases, the compaction mechanism is an integral part of the container. When containers are equipped with a self-contained compaction mechanism, the moveable bulkhead used to compress the wastes is also used to discharge the compacted wastes.

Railroad Transport Renewed interest is developing in the use of railroads for hauling solid wastes, especially in heavily populated areas where landfill space is scarce and tipping fees are high. Containerized waste on "piggyback" rail cars are used. Full-size bulk material cars are also used for shipping solid wastes.

Water Transport Barges, scows, and special boats have been used in the past to transport solid wastes to processing locations and to seaside and ocean disposal sites, but ocean disposal is no longer practiced by the United States. Although some self-propelled vessels (such as U.S. Navy garbage scows and other special boats) have been used, most common practice is to use vessels towed by tugs or other special boats.

Pneumatic Transport Both low-pressure air-vacuum conduit transport systems have been used to transport solid wastes. The most common application is the transport of wastes from high-density apartments or commercial activities to a central location for processing or for loading into transport vehicles. The largest pneumatic system in use in the United States is at the Walt Disney World amusement park in Orlando, Florida.

Location of Transfer Stations Whenever possible, transfer stations should be located (1) as near as possible to the weighted center of the individual solid-waste-production ares to be served, (2) within easy access of major arterial highways as well as near secondary or supplemental means of transportation, (3) where there will be a minimum of public and environmental objection to the transfer operations, and (4) where construction and operation will be most economical. Additionally, if the transfer-station site is to be used for processing operations involving material recovery and/or energy production, the requirements for those operations must be considered.

Transfer and Transport of Hazardous Wastes The facilities of a hazardous-waste transfer station are quite different from those of an industrial or municipal solid-waste transfer station. Typically, hazardous wastes are not compacted (mechanical volume reduction), discharged at differential levels, or delivered by numerous collection companies. Instead, liquid hazardous wastes are generally pumped from collection vehicles, and sludges or solids are reloaded without removal from the collection containers for transport to processing and disposal facilities. Repacking may occur at a TSD (transport, storage, and disposal facility) to put the waste into standard size and weight containers for reshipment to final treatment facilities. Most often, this involves subdividing larger containers into smaller containers and/or use of compatible container material. Examples are the use of fiber drums rather than steel barrels and prepacking to limit the heat content or volatility of waste destined for hazardous waste incineration.

It is unusual to find a hazardous-waste-transfer facility at which wastes are simply transferred to larger transport vehicles. Some processing and storage facilities are often part of the materials-handling sequence at a transfer section. For example, neutralization of corrosive wastes will result in the use of lower-cost holding tanks on transport vehicles.

PROCESSING AND RESOURCE RECOVERY

The purpose of this subsection is to introduce the reader to the techniques and methods used to recover materials, conversion products, and energy from solid wastes. Topics to be considered include (1) processing techniques for solid waste, (2) processing techniques for hazardous wastes, (3) materials-recovery systems, (4) recovery of biological conversion products, (5) thermal processes, and (6) waste-to-energy systems.

Because many of the techniques, especially those associated with the recovery of materials and energy and the processing of solid hazardous wastes, are in a state of flux with respect to application and design criteria, the objective here is only to introduce them to the reader. If these techniques are to be considered in the development of waste-management systems, current engineering design and performance data must be obtained from consultants, operating records, field tests, equipment manufacturers, and available literature.

Processing Techniques for Solid Wastes Processing techniques are used in solid-waste-management systems to (1) improve the efficiency of the systems, (2) to recover resources (usable materials), and (3) to prepare materials for recovery of conversion products and energy. The more important techniques used for processing solid wastes are summarized in Tables 25-61 and 25-62.

Manual Component Separation The manual separation of solid-waste components can be accomplished at the source where solid wastes are generated, at a transfer station, at a centralized processing station, or at the disposal site. Manual sorting at the source of generation is the most positive way to achieve the recovery and reuse of materials. The number and types of components salvaged or sorted (e.g., cardboard and high-quality paper, metals, and wood) depend on the location, the opportunities for recycling, and the resale market. There has been an evolution in the solid waste industry to combine manual and automatic separation techniques to reduce overall costs and produce a cleaner product, especially for recyclable materials.

Storage and Transfer When solid wastes are to be processed for material recovery, storage and transfer facilities should be considered

an essential part of the processing operation. Important factors in the design of such facilities include (1) the size of the material before and after processing, (2) the density of the material, (3) the angle of repose before and after processing, (4) the abrasive characteristics of the material, and (5) the moisture content.

Mechanical Volume Reduction Mechanical volume reduction is perhaps the most important factor in the development and operation of solid-waste-management systems. Vehicles equipped with compaction mechanisms are used for the collection of most industrial solid wastes. To increase the useful life of landfills, wastes are compacted. Paper for recycling is baled for shipping to processing centers. When compacting industrial solid wastes, it has been found that the final density (typically about 1,100 kg/m^3) is essentially the same regardless of the starting density and applied pressure. This fact is important in evaluating manufacturers' claims.

Chemical Volume Reduction Incineration has been the method commonly used to reduce the volume of wastes chemically. One of the most attractive features of the incineration process is that it can be used to reduce the original volume of combustible solid wastes by 80 to 90 percent. The technology of incineration has advanced since 1960 with many mass burn facilities now have two or more combustors with capacities of 1000 tons per day of refuse per unit. However, regulations of metal and dioxin emissions have resulted in higher costs and operating complexity.

Mechanical Size Alteration The objective of size reduction is to obtain a final product that is reasonably uniform and considerably reduced in size in comparison to its original form. It is important to note that size reduction does not necessarily imply volume reduction. In some situations, the total volume of the material after size reduction may be greater than the original volume. Shredding is most often used for size reduction. Use of two-stage (coarse, fine) low-speed shredders or a single-stage shredder with screen and recycle of oversize are the most common systems. The gain in ease of material handling must be weighed against the substantial operating costs for shredding equipment.

Mechanical Component Separation Component separation is a necessary operation in the recovery of resources from solid wastes and in instances when energy and conversion products are to be recovered from processed wastes. Mechanical separation techniques that have been used are reported in Table 25-61.

Magnetic and Electromechanical Separation Magnetic separation of ferrous materials is a well-established technique. More recently, a variety of electromechanical techniques have been developed for the removal of several nonferrous materials (see Table 25-62).

Drying and Dewatering In many solid-waste energy-recovery and incineration systems, the shredded light fraction is predried to decrease weight. Although energy requirements for drying wastes vary with the application, the required energy input can be established by using a value of about 4300 kJ/kg of water evaporated. Drying can frequently increase waste throughput in many treatment systems and for incinerators; it produces more stable combustion and better ash quality.

Processing of Hazardous Wastes As with conventional solid wastes, the processing of hazardous wastes is undertaken for three purposes: (1) to recover useful materials, (2) to reduce the amount of wastes that must be disposed in landfills, and (3) to prepare the wastes for ultimate disposal.

Processing Techniques The processing of hazardous wastes on a batch basis can be accomplished by physical, chemical, thermal, and biological means. The various individual processes in each category are reported in Table 25-63. Clearly, the number of possible treatment-process combinations is staggering. In practice, the physical, chemical, and thermal treatment operations and processes are the ones most commonly used.

Identification of Waste Constituents In any processing (and disposal) scheme, the key item is knowledge of the characteristics of the wastes to be handled. Without this information, effective processing or treatment is impossible. For this reason, the characteristics of the wastes must be known before they are accepted and hauled to a treatment or disposal site. In most states, proper identification of the constituents of the waste is the responsibility of the waste generator.

Materials-Recovery Systems Paper, rubber, plastics, textiles, glass, metals, and organic and inorganic materials are the principal recoverable materials contained in industrial solid wastes.

Once a decision has been made to recover materials and/or energy, process flow sheets must be developed for the removal of the desired components, subject to predetermined materials specifications. A typical flow sheet for the recovery of specific components and the preparation of combustible materials for use as a fuel source is presented in Fig. 25-63. The light combustible materials are often identified as refuse-derived fuel (RDF).

The design and layout of the physical facilities that make up the processing-plant flow sheet are an important aspect in the implementation and successful operation of such systems. Important factors that must be considered in the design and layout of such systems include (1) process performance efficiency, (2) reliability and flexibility, (3) ease and economy of operation, (4) aesthetics, and (5) environmental controls.

Recovery of Biological Conversion Products Biological conversion products that can be derived from solid wastes include compost, methane, various proteins and alcohols, and a variety of other intermediate organic compounds. The principal processes that have been used are reported in Table 25-64. Composting and anaerobic digestion, the two most highly developed processes, are considered further. The recovery of gas from landfills is discussed in the portion of this section dealing with ultimate disposal.

TABLE 25-61 Mechanical Methods for Separating Solid-Waste Components

Method	Function	Equipment and/or facilities and applications	Method	Function
Screening	Used to separate solid waste components by size	Trommels and horizontal and vibrating screens for unprocessed and processed wastes; disk screens with processed wastes	Optical sorting	Used to separate plastics
			Sink-float, flotation, Inertial, Inclined-table, shaking-table	Used to separate light and heavy materials in solid wastes
Air separation	Used to separate light (organic) materials from heavy (inorganic) materials in solid waste	Zig-zag-air, vibrating-air, rotary-air, and air-knife classifiers used with processed wastes		
Jig separation	Used to separate light and heavy materials in solid waste by means of density separation			
Pneumatic separation (stoners)	Used to separate light and heavy materials in solid waste			

TABLE 25-62 Summary of Techniques Used for Processing Solid Wastes

Processing technique	Function	Representative equipment and/or facilities and applications
Manual component separation	Separation of recoverable materials, usually at point of generation	Visual inspection and removal via conveyor belt picking stations
Storage and transfer	Storage and transfer of wastes to be processed	Open storage pits for unprocessed wastes, storage bins and silos for processed wastes; transfer equipment including front-end loaders, metal and rubber belt conveyors, vibratory conveyors with unprocessed wastes, pneumatic conveyors, and screw conveyors with processed wastes
Mechanical volume reduction	Reduction of solid-waste volume; alteration of shape of solid-waste components; all modern collection vehicles essentially equipped with compaction equipment	Hydraulic piston-type compactors for collection vehicles, on-site compactors, and transfer-station compactors; roll crushers used to fracture brittle materials and to crush tin and aluminum cans and other ductile materials
Chemical volume reduction	Reduction of volume of solid wastes through burning (incineration)	Mass-fired incinerators, with and without heat recovery, for unprocessed wastes; rotary kilns for hazardous/containerized and bulk solid/sludge waste
Mechanical size and shape alteration	Alteration of size and shape of solid-waste components	Equipment used to reduce the size of solid waste including hammer mills, shredders, roll crushers, grinders, chippers, jaw crushers, rasp mills, and hydropulpers; briquettes
Mechanical component separation	Separation of recoverable materials, usually at a processing facility	(See Table 26-40)
Magnetic and electromechanical separation	Separation of ferrous and nonferrous materials from processed solid wastes	Magnetic separation for ferrous materials; eddy-current separation for aluminum; electrostatic separation for glass from wastes free of ferrous and aluminum scrap; magnetic fluid separation for nonferrous materials from processed wastes
Drying and dewatering	Removal of moisture from solid wastes	Convection, conduction, and radiation dryers used for solid wastes and sludge; centrifuge and filtration used to dewater treatment-plant sludge

Composting If the organic materials, excluding plastics, rubber, and leather, are separated from municipal solid wastes and subjected to bacterial decomposition, the end product remaining after dissimilatory and assimilatory bacterial activity is called *compost* or *humus*. The entire process involving both separation and bacterial conversion of the organic solid wastes is known as *composting*. Decomposition of the organic solid wastes may be accomplished either aerobically or anaerobically, depending on the availability of oxygen.

Most composting operations involve three basic steps: (1) preparation of solid wastes, (2) decomposition of the solid wastes, and (3) product preparation and marketing. Receiving, sorting, separation, size reduction, and moisture and nutrient addition are part of the preparation step. Several techniques have been developed to accomplish the decomposition step. Once the solid wastes have been converted to a humus, they are ready for the third step of product preparation and marketing. This step may include fine grinding, blending with various additives, granulation, bagging, storage, shipping, and, in some cases, direct marketing. The principal design considerations associated with the biological decomposition of prepared solid wastes are presented in Table 25-65.

Anaerobic Digestion Anaerobic digestion or anaerobic fermentation, as it is often called, is the process used for the production of methane from solid wastes. In most processes in which methane is to be produced from solid wastes by anaerobic digestion, three basic steps are involved. The first step involves preparation of the organic fraction of the solid wastes for anaerobic digestion and usually includes receiving, sorting, separation, and size reduction. The second step involves the addition of moisture and nutrients, blending, pH adjustment to about 6.7, heating of the slurry to between 327 and 333 K (130 and 140° F), and anaerobic digestion in a reactor with continuous flow, in which the contents are well mixed for a period of time varying from 8 to 15 days. The third step involves capture, storage, and, if necessary, separation of the gas components evolved during the digestion process. The fourth step is the disposal of the digested sludge is an additional task that must be accomplished. Some important design considerations are reported in Table 25-66. Because of the variability of the results reported in the literature, it is recommended that pilot-plant studies be conducted if the digestion process is to be used for the conversion of solid wastes.

Thermal Processes Conversion products that can be derived from solid wastes include heat, gases, a variety of oils, and various related organic compounds. The principal thermal processes that have been used for the recovery of usable conversion products from solid wastes are reported in Table 25-64.

Incineration with Heat Recovery Heat contained in the gases produced from the incineration of solid wastes can be recovered as steam. The low-level heat remaining in the gases after heat recovery can also be used to preheat the combustion air, boiler makeup water, or solid-waste fuel.

1. *In existing incinerators.* With existing incinerators, waste-heat boilers can be installed to extract heat from the combustion gases without introducing excess amounts of air or moisture. Typically, incinerator gases will be cooled from a range of 1250 to 1375 K (1800 to 2000° F) to a range from 500 to 800 K (600 to 1000° F) before being discharged to the air pollution control system. Apart from the production of steam, the use of a boiler system is beneficial in reducing the volume of gas to be processed in the air-pollution-control equipment. The compounds in the waste stream will generate products of combustion and ash that may create serious corrosion and fouling problems in waste-heat boilers.

2. *In water-wall incinerators.* The internal walls of the combustion chamber are lined with boiler tubes that are arranged vertically and welded together in continuous sections. When water walls are employed in place of refractory materials, they are not only useful for the recovery of steam but also extremely effective in controlling furnace temperature without introducing excess air; however, they are subject to corrosion by the hydrochloric acid produced from the burning of some plastic compounds and the molten ash containing salts (chlorides and sulfates) that attach to the tubes.

Combustion Combustion of industrial and municipal waste is an attractive waste management option because it reduces the volume of waste by 70 to 90 percent. In the face of shrinking landfill availability, municipal waste combustion capacity in the United States has grown at an astonishing rate, significantly faster than the growth rate for municipal refuse generation.

Types of Combustors The three main classes of facilities used to combust municipal refuse are mass burn, modular, and RDF-fired facilities. Mass-burn combustors are field erected and generally range in size from 50 to 1000 tons/day of refuse feed per unit (Fig. 25-64). Modular combustors burn waste with little more pre-

TABLE 25-63 Treatment Operations and Processes for Hazardous Wastes[a]

Operation or process	Functions performed[b]	Types of wastes[c]	Forms of waste[d]
Physical treatment			
Adsorption[e]	Se	1, 2, 3,	L
Aeration	Se	1, 2, 3, 4, 5	L
Ammonia stripping	VR, Se	1, 2, 3, 4	L
Carbon sorption	VR, Se	1, 2, 3, 4, 5	L, G
Centrifugation	VR, Se	1, 2, 3, 4, 5	L
Dialysis	VR, Se	1, 2, 3, 4	L
Distillation[e]	VR, Se	1, 2, 3, 4, 5	L
Electrodialysis	VR, Se	1, 2, 3, 4, 6	L
Encapsulation	St	1, 2, 3, 4, 6	L, S
Evaporation	VR, Se	1, 2, 5	L
Filtration[e]	VR, Se	1, 2, 3, 4, 5	L, G
Flocculation or setting	VR, Se	1, 2, 3, 4, 5	L
Flotation[e]	Se	1, 2, 3, 4	L
Reverse osmosis	VR, Se	1, 2, 4, 6	L
Screening	Se	1, 2, 3, 4, 5	L
Sedimentation[e]	VR, Se	1, 2, 3, 4, 5	L
Shredding	VR, Se	1, 2, 3, 4	S
Solar evaporation[e]	VR, Se	1, 2, 5	L
Solvent extraction	Se	1, 2, 3, 4, 5	L
Thickening	Se	1, 2, 3, 4	L
Ultrafiltration	Se	1, 2, 3, 4, 5	L
Vapor scrubbing	VR, Se	1, 2, 3, 4	L
Chemical treatment			
Calcination	VR	1, 2, 5	L
Chemical dechlorination	De	1, 3	L
Ion exchange	VR, Se, De	1, 2, 3, 4, 5	L
Neutralization[e]	De	1, 2, 3, 4	L
Oxidation	De	1, 2, 3, 4	L
Precipitation[e]	VR, Se	1, 2, 3, 4, 5	L
Reduction	De	1, 2	L
Sorption	De	1, 2, 3, 4	L
Stabilization or solidification[e]	De	1, 2, 3, 4	L
Thermal treatment			
Desorption	VR, De	1, 2, 3, 4	S
Incineration[e]	VR, De	3, 5, 6, 7, 8	S, L, G
Pyrolysis	VR, De	3, 4, 6	S, L, G
Biological treatment			
Activated sludge[e]	De	3	L
Aerated lagoons	De	3	L
Anaerobic digestion	De	3	L
Anaerobic filters	De	3	L
Trickling filters	De	3	L
Waste-stabilization ponds[e]	De	3	L

[a]Adapted from *Report to Congress: Disposal of Hazardous Wastes,* U.S. EPA Publ. SW-115, 1974.
[b]Functions: VR, volume reduction; Se, separation; De, detoxification; St, storage.
[c]Waste types: 1, inorganic chemical without heavy metals; 2, inorganic chemical with heavy metals; 3, organic chemical without heavy metals; 4, organic chemical with heavy metals; 5, radiological; 6, biological; 7, flammable; 8, explosive.
[d]Waste forms: S, solid; L, liquid; G, gas.
[e]Most widely used technologies for hazardous-waste management.

processing than do the mass-burn units. These range in size from 5 to 100 tons/day. The third major class of municipal waste combustor burns RDF. The types of waste-to-energy boilers used to combust RDF can include suspension, stoker, and fluidized bed designs. RDF fuels can also be fired directly in large industrial boilers that are now used for the production of power with pulverized or stoker coal, oil, and gas. Although the process is not well established with coal, it appears that about 15 to 20 percent of the heat input can be from RDF. With oil as the fuel, about 10 percent of the heat input can be from RDF. Depending on the degree of processing, suspension, spreader-stoker, and double-vortex firing systems have been used.

Gasification The gasification process involves the partial combustion of a carbonaceous or hydrocarbon fuel to generate a combustible fuel gas rich in carbon monoxide and hydrogen. A gasifier is basically an incinerator operating under reducing conditions. Heat to sustain the process is derived from exothermic reactions, while the combustible components of the low-energy gas are primarily generated by endothermic reactions. The reaction kinetics of the gasification process are quite complex and still the subject of considerable debate.

When a gasifier is operated at atmospheric pressure with air as the oxidant, the end products of the gasification process are a low-energy gas typically containing (by volume) 10 percent CO_2, 20 percent CO, 15 percent H_2, and 2 percent CH_4, with the balance being N_2, and a carbon-rich ash. Because of the diluting effect of the nitrogen in the input air, the low-energy gas has an energy content in the range of the 5.2 to 6.0 MJ/m^3 (140 to 160 Btu/ft^3). When pure oxygen is used as the oxidant, a medium-energy gas with an energy content in the range of 12.9 to 13.8 MJ/m^3 (345 to 370 Btu/ft^3) is produced. Gasifiers were in widespread use on coal and wood until natural gas displaced them in the 1930s–1950s. Some large coal gasifiers are in use today in the United States and worldwide. While the process can work on solid waste, incinerators (which gasify and burn in one chamber) are favored over gasifiers.

Pyrolysis Of the many alternative chemical conversion processes that have been investigated, pyrolysis has received the most attention. Pyrolysis has been tested in countless pilot plants, and many full-scale demonstration systems have been operated. Few attained any long-term commercial use. Major issues were lack of market for the unstable and acidic pyrolytic oils and the char.

Depending on the type of reactor used, the physical form of solid wastes to be pyrolized can vary from unshredded raw wastes to the finely ground portion of the wastes remaining after two stages of shredding and air classification. Upon heating in an oxygen-free atmosphere, most organic substances can be split via thermal cracking and condensation reactions into gaseous, liquid, and solid fractions. Pyrolysis is the term used to describe the process. In contrast to the combustion process, which is highly exothermic, the pyrolytic process is highly endothermic. For this reason, the term *destructive distillation* is often used as an alternative for *pyrolysis.*

The characteristics of the three major component fractions resulting from the pyrolysis are (1) a gas stream containing primarily hydrogen, methane, carbon monoxide, carbon dioxide, and various other gases, depending on the organic characteristics of the material being pyrolyzed; (2) a fraction that consists of a tar and/or oil stream that is liquid at room temperatures and has been found to contain hundreds of chemicals such as acetic acid, acetone, methanol, and phenols; and (3) a char consisting of almost pure carbon plus any inert material that may have entered the process. It has been found that distribution of the product fractions varies with the temperature at which the pyrolysis is carried out. Under conditions of maximum gasification, the energy content of the resulting gas is about 26.1 MJ/kg (700 Btu/ft^3). The energy content of pyrolytic oils has been estimated to be about 23.2 MJ/kg (10,000 Btu/lb).

Waste-to-Energy Systems The preceding section ended at production of steam. WTE (waste-to-energy) systems take over at this point, using high-pressure/high-temperature steam to drive turbines and produce shaft horsepower for prime movers at industrial plants or to generate electricity.

The fuel may be solid waste or gas or oil from a gasifier or pyrolysis system.

Typical flow sheets for alternative energy-recovery systems are shown in Fig. 25-65. Perhaps the most common flow sheet for the production of electric energy involves the use of a steam turbine-generator combination (see Fig. 25-65). As shown, when solid wastes are used as the basic fuel source, four operating modes are possible. A flow sheet using a gas-turbine-generator combination is shown in Fig. 25-65. The low-energy gas is compressed under high pressure so that it can be used more effectively in the gas turbine. Use of low- or medium-Btu gas for gas turbines has been attempted, and success requires good design and operation of gas cleaning equipment prior to introduction into the combustor of the gas turbine.

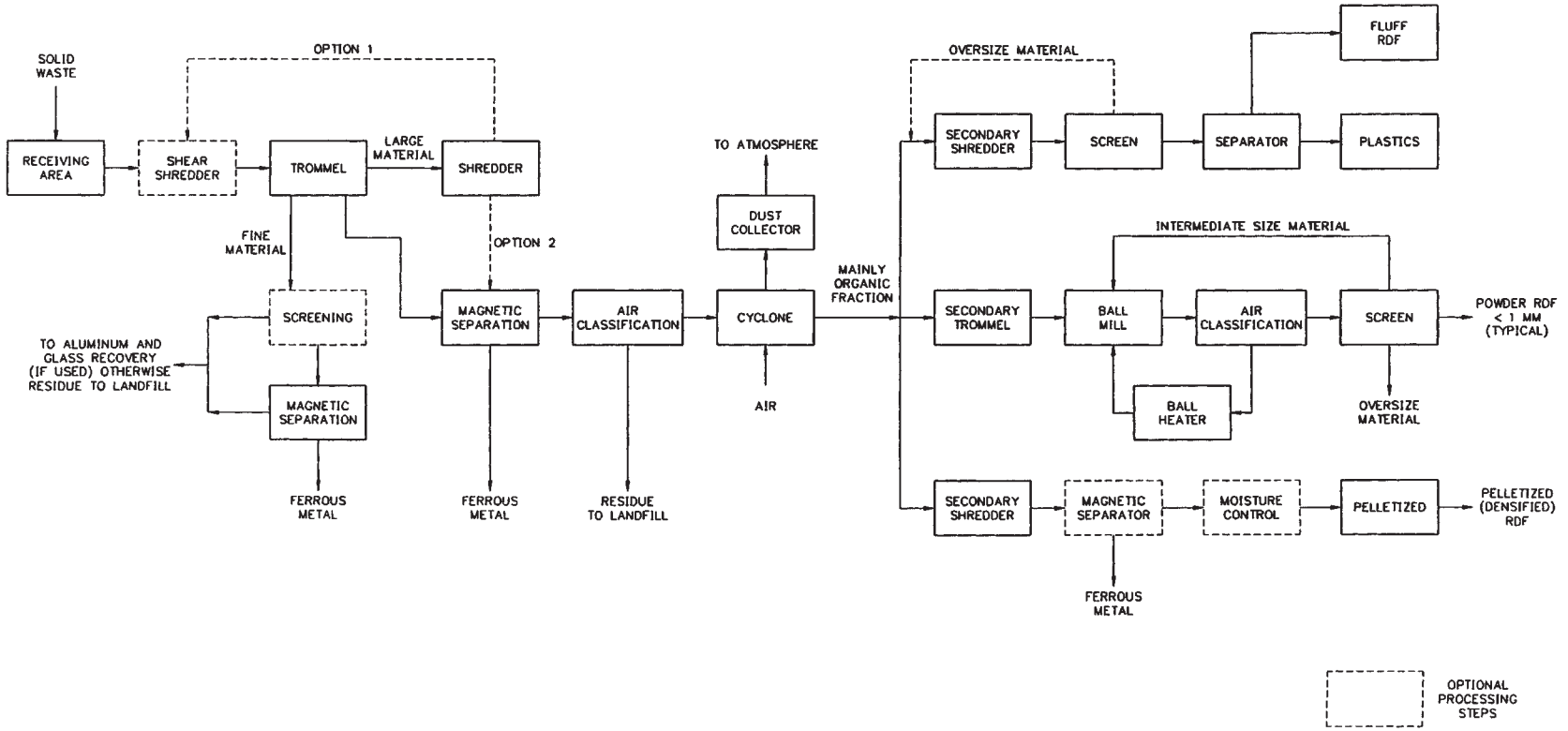


FIG. 25-63 Typical flow sheet for the recovery of materials and production of refuse-derived fuels (RDF). [*Adapted in part from D. C. Wilson (ed.),* Waste Management: Planning, Evaluation, Technologies, *Oxford University Press, Oxford, 1981.*]

TABLE 25-64 Biological and Thermal Processes Used for Recovery of Conversion Products from Solid Waste

Process	Conversion product	Preprocessing required	Comments
Biological			
Composting	Humuslike material	Shredding, air separation	Lack of markets primary shortcoming; technically proven in full-scale application
Anaerobic digestion	Methane gas	Shredding, air separation	Technology on laboratory scale only
Biological conversion to protein	Protein, alcohol	Shredding, air separation	Technology on pilot scale only
Biological fermentation	Glucose, furfural	Shredding, air separation	Used in conjunction with the hydrolytic process
Thermal			
Incineration with heat recovery	Energy in the form of steam	None	Markets for steam required; proven in numerous full-scale applications; air-quality regulations possibly prohibiting use
Supplementary fuel firing in boilers	Energy in the form of steam	Shredding, air separation, magnetic separation	If least capital investment desired, existing boiler required to be capable of modification; air-quality regulations possibly prohibiting use
Gasification	Energy in the form of low energy gas	Shredding, air separation, magnetic separation	Gasification also capable of being used for codisposal for industrial sludges
Pyrolysis	Energy in the form of gas or oil	Shredding, magnetic separation	Technology proven only in pilot applications; even though pollution is minimized, air-quality regulations possibly prohibiting use
Hydrolysis	Glucose, furfural	Shredding, air separation	Technology on pilot scale only
Chemical conversion	Oil, gas, cellulose acetate	Shredding, air separation	Technology on pilot scale only

TABLE 25-65 Important Design Considerations for Aerobic-Composting Processes*

Item	Comment
Particle size	For optimum results the size of solid wastes should be between 25 and 75 mm (1 and 3 in).
Seeding and mixing	Composting time can be reduced by seeding with partially decomposed solid wastes to the extent of about 1 to 5 percent by weight. Sewage sludge can also be added to prepared solid wastes. When sludge is added, the final moisture content is the controlling variable.
Mixing or turning	To prevent drying, caking, and air channeling, material in the process of being composted should be mixed or turned on a regular schedule or as required. Frequency of mixing or turning will depend on the type of composting operation.
Air requirements	Air with at least 50 percent of the initial oxygen concentration remaining should reach all parts of the composting material for optimum results, especially in mechanical systems.
Total oxygen requirements	The theoretical quantity of oxygen required can be estimated.
Moisture content	Moisture content should be in the range between 50 and 60 percent during the composting process. The optimum value appears to be about 55 percent.
Temperature	For best results temperature should be maintained between 322 and 327 K (130 and 140°F) for the first few days and between 327 and 333 K (130 and 140°F) for the remainder of the active composting period. If temperature goes beyond 339 K (150°F), biological activity is reduced significantly.
Carbon-nitrogen ratio	Initial carbon-nitrogen ratios (by mass) between 35 and 50 are optimum for aerobic composting. At lower ratios ammonia is given off. Biological activity is also impeded at lower ratios. At higher ratios nitrogen may be a limiting nutrient.
pH	To minimize the loss of nitrogen in the form of ammonia gas, pH should not rise above about 8.5.
Control of pathogens	If the process is properly conducted, it is possible to kill all the pathogens, weeds, and seeds during the composting process. To do this, the temperature must be maintained between 333 and 344 K (140 and 160°F) for 24 h.

*Adapted from G. Tchobanoglous, H. Theisen, R. Eliassen, *Solid Wastes: Engineering Principles and Management Issues,* McGraw-Hill, New York, 1977.

Efficiency Factors Representative efficiency data for boilers, pyrolytic reactors, gas turbines, steam-turbine-generator combinations, electric generators, and related plant use and loss factors are given in Table 25-67. In any installation in which energy is being produced, allowance must be made for the power needs of the station or process and for unaccounted-for-process-heat losses. Typically, the auxiliary power allowance varies from 4 to 8 percent of the power produced. Process-heat losses usually will vary from 2 to 8 percent. In general, steam pressures of 600 psig and temperatures of 650° F are considered minimum for economical power generation. Industrial plants may choose a cogeneration topping cycle, with steam exhaust from the turbine at the plant's process steam pressure, typically in the 125–250-psig range. For commercial WTE plants, condensing turbines are the norm.

Determination of Energy Output and Efficiency for Energy-Recovery Systems An analysis of the amount of energy produced

TABLE 25-66 Important Design Considerations for Anaerobic Digestion*

Item	Comment
Size of material shredded	Wastes to be digested should be shredded to a size that will not interfere with the efficient functioning of pumping and mixing operations.
Mixing equipment	To achieve optimum results and to avoid scum buildup, mechanical mixing is recommended.
Percentage of solid wastes mixed with sludge	Although amounts of waste varying from 50 to 90+ percent have been used, 60 percent appears to be a reasonable compromise.
Hydraulic and mean cell residence time, $\Theta_h = \Theta_c$	Washout time is in the range of 3 to 4 days. Use 8 to 15 days for design or base design on results of pilot-plant studies.
Loading rate	0.6 to 1.6 kg/(m^3·day) [0.04 to 0.10 lb/(ft^3·day)]. Not well defined at present time. Significantly higher rates have been reported.
Temperature	Between 327 and 333 K (130 and 140°F).
Destruction of volatile solid wastes	Varies from about 60 to 80 percent; 70 percent can be used for estimating purposes.
Total solids destroyed	Varies from 40 to 60 percent, depending on amount of inert material present originally.
Gas production	0.5 to 0.75 m^3/kg (8 to 12 ft^3/lb) of volatile solids destroyed (CH_4 = 60 percent; CO_2 = 40 percent).

*From G. Tchobanoglous, H. Theisen, and R. Eliassen, *Solid Wastes: Engineering Principles and Management Issues,* McGraw-Hill, New York, 1977.

†Actual removal rates for volatile solids may be less, depending on the amount of material diverted to the scum layer.

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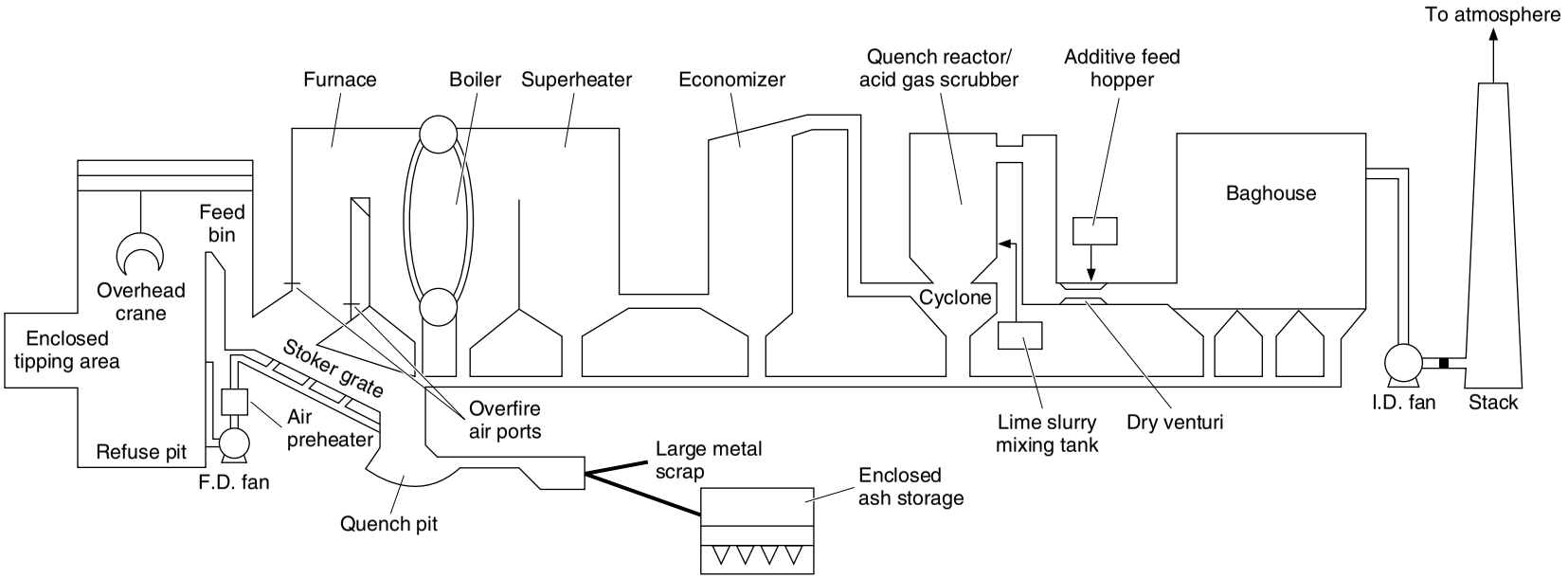
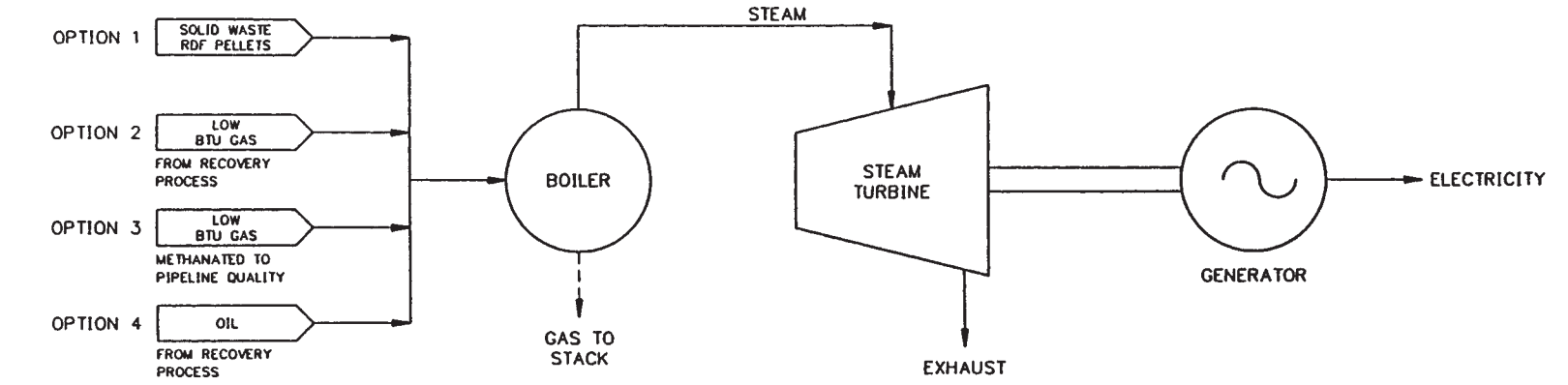


FIG. 25-64 Diagram of a modern mass-burn facility. *(From Municipal Waste Combustion Study Report to Congress, June 1982, PB87-206074.)*



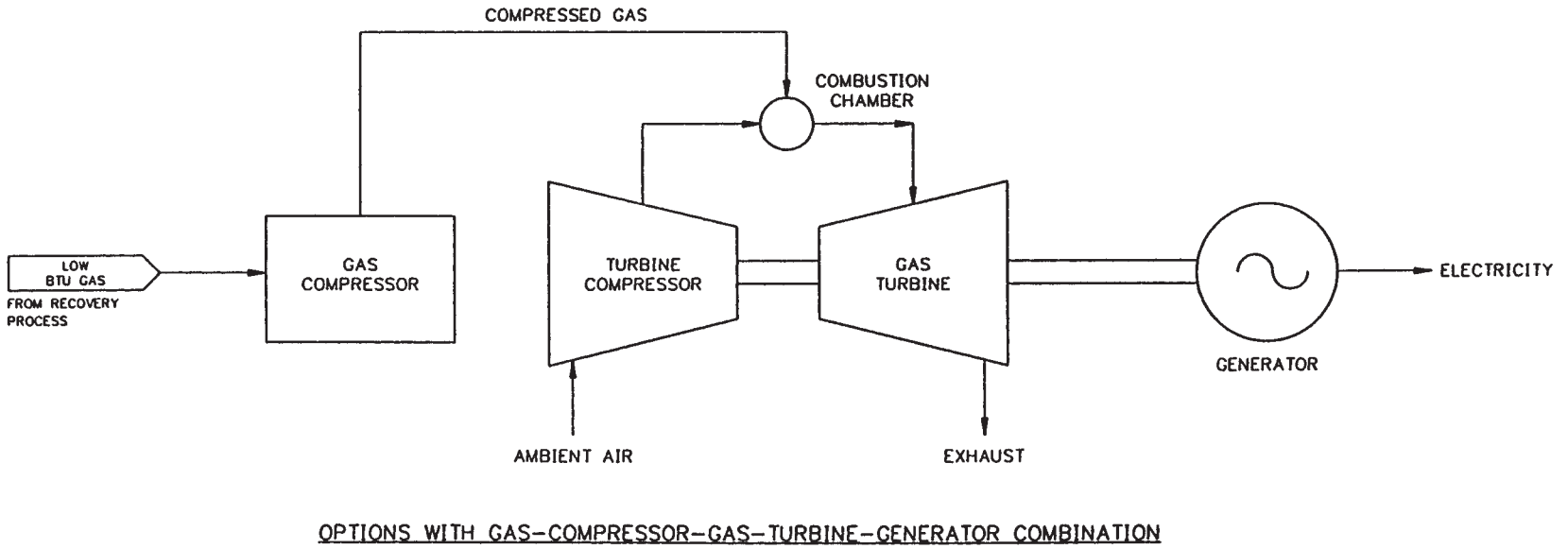


FIG. 25-65 Flow sheet—alternative energy recovery systems.

TABLE 25-67 Typical Thermal Efficiency and Plant Use and Loss Factors for Individual Components and Processes Used for Recovery of Energy from Solid Wastes

Component	Efficiency*		Comments
	Range	Typical	
Incinerator-boiler	40–68	63	Mass-fired
Boiler			
Solid fuel	60–75	72	Processed solid wastes (RDF)
Low-Btu gas	60–80	75	Necessity to modify burners
Oil-fired	65–85	80	Oils produced from solid wastes possibly required to be blended to reduce corrosiveness
Gasifier	60–70	70	
Pyrolysis reactor	65–75	70	
Turbines			
Combustion gas			
Simple cycle	8–12	10	
Regenerative	20–26	24	Including necessary appurtenances
Expansion gas	30–50	40	
Steam-turbine-generator system			
Less than 10 MW	24–40	29†‡	Including condenser, heaters, and all other necessary appurtenances but not boiler
Over 10 MW	28–32	31.6†‡	
Electric generator			
Less than 10 MW	88–92	90	
Over 10 MW	94–98	96	
Plant use and loss factors			
Station-service allowance			
Steam-turbine-generator plant	4–8	6	
Unaccounted heat losses	2–8	5	

*Theoretical value for mechanical equivalent of heat = 3600 kJ/kWh.
†Efficiency varies with exhaust pressure. Typical value given is based on an exhaust pressure in the range of 50 to 100 mmHg.
‡Heat rate = 11,395 kJ/kWh = (3600 kJ/kWh)/0.316.

TABLE 25-68 Energy Output and Efficiency for 1000 Metric Ton of Waste/Day Steam-Boiler Turbine-Generator Energy-Recovery Plant Using Unprocessed Industrial Solid Wastes with Energy Content of 12,000 kJ/kg

Item	Value
Energy available in solid wastes, million kJ/h [(1000 metric tons/day × 1000 kg/metric ton × 12,000 kJ/kg)/(24h/day × 10^6 kJ/million kJ)]	500
Steam energy available, million kJ/h (500 million kJ/h × 0.7)	350
Electric power generation, kW (350 million kJ/h)/(11,395 kJ/kWh)*	30,715
Station-service allowance, kW [30,715 (0.06)]	−1,843
Unaccounted heat losses, kW [30,715 (0.05)]	−1,536
Net electric power for export, kW	27,336
Overall efficiency, percent {(27,336 kW)/[(500,000,000 kJ/h)/(3,600 kJ/kWh)]}(100)	19.7

*11,395 kJ/kWh = (3600 kJ/kWh)/0.316.

from a solid-waste energy conversion system using an incinerator-boiler-steam-turbine-electric-generator combination with a capacity of 1000 metric tons per day of waste is presented in Table 25-68. If it is assumed that 10 percent of the power generated is used for the front-end processing system (typical values vary from 8 to 14 percent), then the net power for export is 24,604 kW and the overall efficiency is 17.5 percent.

Concentration of WTE Incinerators The total number of municipal waste incinerator facilities as listed in the *Solid Waste Digest,* vol. 4, no. 9 September 1994 (a publication of Chartwell Information Publishers of Alexandria, VA) is 62. See Table 25-69, which covers over 200 existing units. The wastes burned in these facilities totals 8.44 percent of total municipal wastes managed in landfills, incinerators, and transfer stations. This amounts to 88,470 tons per day combusted municipal waste.

One notes that the heavily populated areas of the country also have the highest number of WTE facilities as well as the highest intake of municipal waste into incinerators. This is also due to the lack of open space for landfills compared to the midwest and western states. The amount of waste combusted in the northeastern states is 20.7 percent of the total generated compared to 8.44 percent of all municipal wastes combusted nationwide. The cost per ton averages $77 in New Jersey and New York compared to $57 for the nation. Incinerator costs are similar to landfill costs in the northeastern states. However, landfill costs are far lower than WTE tipping fees. For example, in states like Idaho (landfill costs, $12/ton) and Texas (landfill costs, $10/ton), WTE incinerator plants cannot compete. The NIMBY (Not in my Backyard) syndrome concerning incineration systems has also hurt the siting and permitting of many of these facilities. Figure 25-66 shows the range of costs for incineration in September 1994. Figure 25-67 shows the range costs for all solid waste management in September 1994. The National index was $37.93/ton in 1994, up from $33.64/ton in 1992. This is an average increase of 6.5% per year which is above the inflation rate for this two-year period.

REGULATIONS APPLICABLE TO MUNICIPAL WASTE COMBUSTORS

New Source Performance Standards (NSPS) were promulgated under Sections 111(b) and 129 of the CAA Amendments of 1990. The NSPS applies to new municipal solid-waste combustors (MWCs) with

TABLE 25-69 Solid Waste Price Index, WTE Incinerator Intake TPD-Tip Fee, September 1994

Region	Number of facilities	Intake, TPD	% of daily intake	Tip fee, $/ton
Northeastern states				
Connecticut	5	6410	60.63	66.35
Delaware	0	0	0	n/a
Massachusetts	2	2460	13.33	60.52
Maryland	3	3562	19.78	64.65
Maine	3	2407	77.94	61.55
New Hampshire	1	997	19.76	52.70
New Jersey	4	6575	22.64	80.40
New York	8	14,150	29.22	74.22
Pennsylvania	6	7580	10.32	62.57
Rhode Island	0	0	0	n/a
Vermont	0	0	0	n/a
Total northeastern states	32	44,141	20.7	66.56
Southern states				
Alabama	1	690	6.39	39.00
Arkansas	0	0	0	n/a
Florida	10	16,633	26.08	58.20
Georgia	0	0	0	n/a
Kentucky	0	0	0	n/a
Louisiana	0	0	0	n/a
Mississippi	0	0	0	n/a
North Carolina	0	0	0	n/a
South Carolina	1	600	4.44	51.50
Tennessee	2	1970	9.81	28.64
Virginia	3	4975	11.12	45.04
West Virginia	0	0	0	n/a
Total southern states	17	24,868	10.32	52.53
Midwestern states				
Iowa	0	0	0	n/a
Illinois	0	0	0	n/a
Indiana	1	2362	6.45	25.00
Kansas	0	0	0	n/a
Michigan	1	1630	5.22	52.66
Minnesota	3	5187	35.4	61.56
Missouri	0	0	0	n/a
North Dakota	0	0	0	n/a
Nebraska	0	0	0	n/a
Ohio	4	5437	9.16	31.32
South Dakota	0	0	0	n/a
Wisconsin	0	0	0	n/a
Total midwestern states	9	14,616	5.89	43.41
Western states				
Arizona	0	0	0	n/a
Colorado	0	0	0	n/a
Idaho	0	0	0	n/a
Montana	0	0	0	n/a
New Mexico	0	0	0	n/a
Nevada	0	0	0	n/a
Oklahoma	1	1230	15.1	41.91
Texas	0	0	0	n/a
Utah	0	0	0	n/a
Wyoming	0	0	0	41.91
Total western states	1	1230	0.76	41.91
Pacific states				
Alaska	0	0	0	n/a
California	2	2673	1.79	27.50
Hawaii	0	0	0	n/a
Oregon	0	0	0	n/a
Washington	1	944	5	87.61
Total Pacific states	3	3617	1.95	43.91
National total	62	88,471	8.44	57.49

capacity to combust more than 250 tons per day of municipal solid waste that commenced construction after December 20, 1989. The proposed standards and guidelines were published in the *Federal Register* on December 20, 1989.

Section 129 of the CAAA of 1990 applies to a range of solid waste incinerators including MWCs, medical waste incinerators (MWIs) and industrial waste incinerators. Incinerators for hazardous solid and liquid wastes are covered under RCRA regulations (40 CFR Parts 260 through 272) and TSCA, Toxic Substances Control Act, 1976 (40 CFR Parts #700–766).

Regulated Pollutants The NSPS regulates MWC emissions, and nitrogen oxides (NO_x) emissions from individual MWC units larger

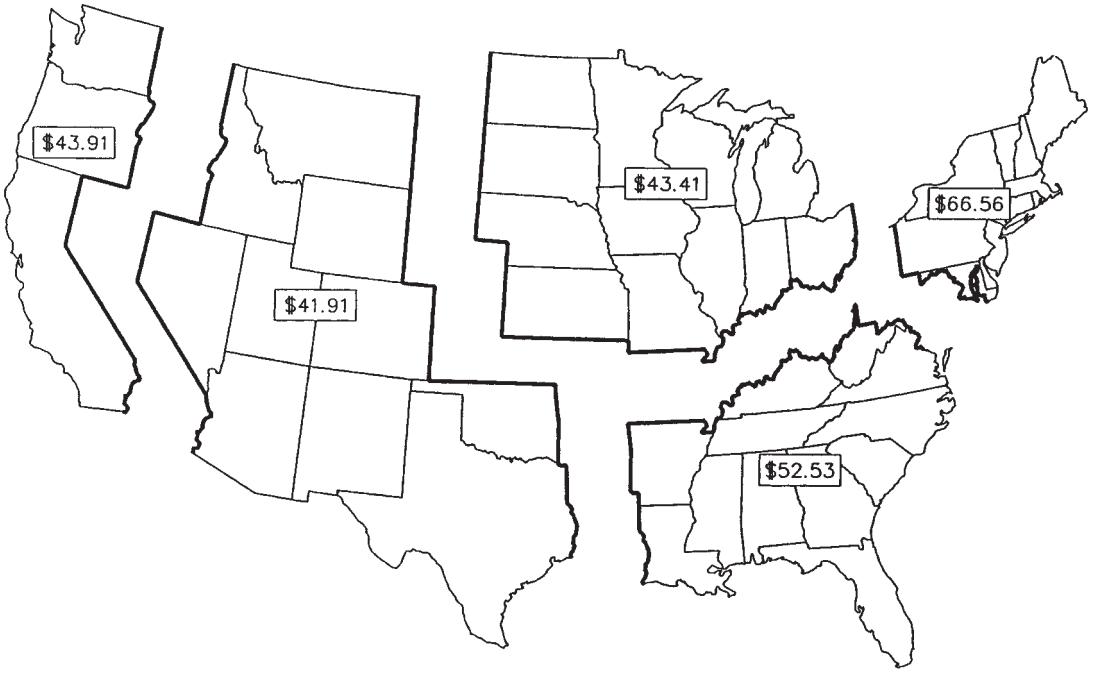


FIG. 25-66 Waste-to-energy price index. National index, September 1994, $57.49/ton. (*Data from* Solid Waste Digest, *vol. 4, no. 9, Sept. 1994. Published by Chartwell Information Publishers, Alexandria, VA.*)

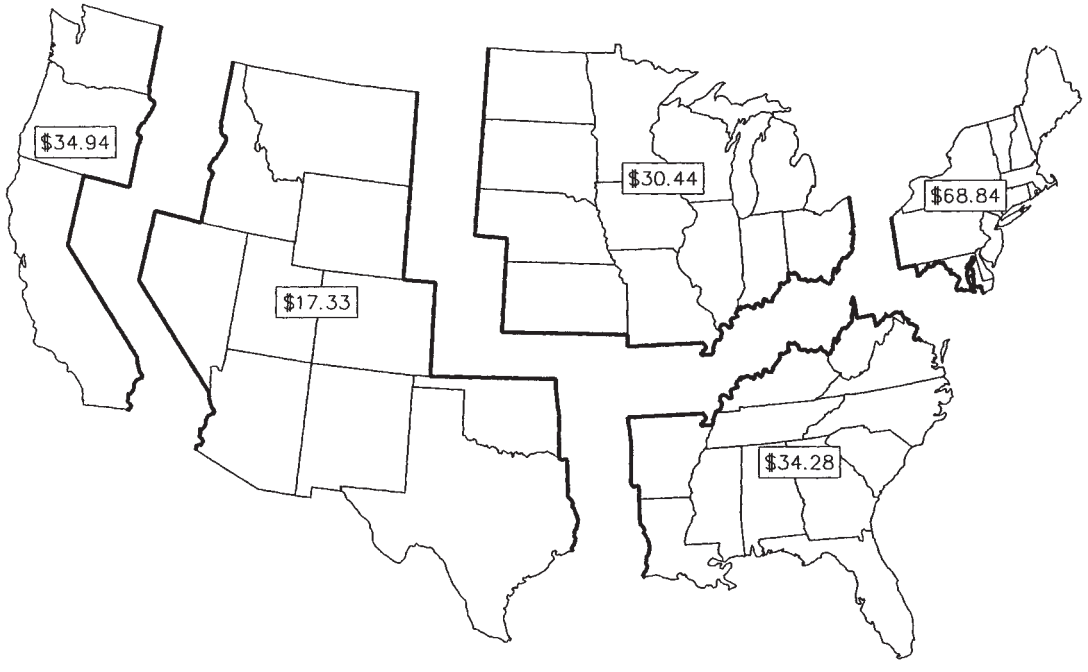


FIG. 25-67 Solid Waste Price Index™. National index, September 1994, $37.93/ton; September 1992, $33.64/ton. (*Data from* Solid Waste Digest, *vol. 4, no. 9, Sept. 1994. Published by Chartwell Information Publishers, Alexandria, VA.*)

than 250 tpd capacity. MWC emissions are subcategorized as MWC metal emissions, MWC organic emissions, and MWC acid gas emissions. The NSPS establishes emission limits for organic emissions (measured as dioxins and furans), MWC metal emissions (measured as particulate matter [PM]), and MWC acid gas emissions (measured as sulfur dioxide [SO_2] and hydrogen chloride [HCl]), as well as NO_x emission limits.

MWCs Organic Emissions The NSPS limits organic emissions to a total dioxin plus furan emission limit of 30 ng/dscm (at 7 percent O_2 dry volume). This level is approximately equivalent to a toxic equivalent (TEQ) of 1.0 ng/dscm, using the 1990 international toxic equivalency factor (I-TEF) approach.

MWCs Metal Emissions The NSPS includes a PM emission limit of 0.015 grains per dry standard cubic feet (gr/dscf) at 7 percent oxygen dry/volume and an opacity limit of 10 percent (6 minute average).

MWCs Acid Gas Emissions The NSPS requires a 95 percent reduction of HCl emissions and an 80 percent reduction of SO_2 emissions for new MWCs or an emission limit of 25 ppmv for HCl and 30 ppmv for SO_2 (at 7 percent O_2 dv).

Nitrogen Oxides Emissions The NSPS limits NO_x emissions to 180 ppmv (at 7 percent O_2 dv).

MSC Air-Pollution-Control Systems MSCs generate flue gas that contains particulates, acid gases and trace amounts of organic and volatile metals. Particulates have traditionally been removed by use of cyclone separators and electrostatic precipitators. Acid gases require neutralization and removal from the gas stream. This can be accomplished by adding solutions or chemicals to the gas stream and removing the products of the chemical reaction when these materials are mixed together. Two major types of APCs are employed:

- Dry systems, where the gas stream is humidified and chemicals are added to the system
- Wet systems, where large quantities of water containing chemicals wash the gas stream

Incinerator Performance Environmental organizations have had concerns regarding performance of existing incineration plants. Major concerns focus on dioxin, mercury, and ash. Groups opposing a proposed WTE facility in New York State set emission standards for the facility. Table 25-70 compares the recommendations for emission levels made by the Natural Resources Defense Council, Environmental Defense Fund, INFORM, Environmental Action Coalition, and Scenic Hudson in *A Solid Waste Blue Print for New York State,* (March, 1988), New York State regulations (GNYCRR Part 219), and actual tests performed at Hempstead in the summer of 1990. Note that the results from the Hempstead stack testing performed in August, 1990 exceed the New York State regulations as well as the environmentalist's recommendation in every category. This was not necessarily true in the case of many MSC plants without proper combustion controls or APC systems. With the standards established in Section 129 of the CAAA of 1990, all facilities must retrofit to conform to these standards or be shut down.

MSC Facilities are required to meet some of the toughest environmental air emission standards in the country. Complying with these standards makes modern waste combustors among the cleanest producers of electricity—and may even provide a means of improving a community's overall air quality.

ULTIMATE DISPOSAL

Disposal on or in the earth's mantle is, at present, the only viable method for the long-term handling of (1) solid wastes that are collected and are of no further use, (2) the residual matter remaining after solid wastes have been processed, and (3) the residual matter remaining after the recovery of conversion products and/or energy has been accomplished. The three land disposal methods used most commonly are (1) landfilling, (2) landfarming, and (3) deepwell injection. Although incineration is being used more often as a disposal method, it is, in reality, a processing method. Recently, the concept of using muds in the ocean floor as a waste-storage location also has received some attention.

Landfilling of Solid Wastes Landfilling involves the controlled disposal of solid wastes on or in the upper layer of the earth's mantle. Important aspects in the implementation of sanitary landfills include (1) site selection, (2) landfilling methods and operations, (3) occurrence of gases and leachate in landfills, (4) movement and control of landfill gases and leachate, and (5) landfill design. The landfilling of hazardous wastes is considered separately.

Site Selection Factors that must be considered in evaluating potential solid-waste-disposal sites are summarized in Table 25-71. Final selection of a disposal site usually is based on the results of a preliminary site survey, results of engineering design and cost studies, and an environmental-impact assessment.

Landfilling Methods and Operations To use the available area at a landfill site effectively, a plan of operation for the placement of solid wastes must be prepared. Various operational methods have been developed primarily on the basis of field experience. The principal methods used for landfilling dry areas may be classified as (1) area, and (2) depression.

1. *Area method.* The area method is used when the terrain is unsuitable for the excavation of trenches in which to place the solid wastes. The filling operation usually is started by building an earthen levee against which wastes are placed in thin layers and compacted (see Fig. 25-68). Each layer is compacted as the filling progresses until the thickness of the compacted wastes reaches a height varying from 2 to 3 m (6 to 10 ft). At that time and at the end of each day's operation, a 150- to 300-mm (6- to 12-in) layer of cover material is placed

TABLE 25-70 Hempstead Emissions Comparison

Parameter*	Environmentalists recommendations	New York State regulations	Actual test results from Hempstead
Particulates (gr/dscf)	0.010	0.010	0.00053
Opacity (clarity of air from the stack)	5%	10%	<5%
Dioxin† (ng/dscm)	0.1	0.2 (goal)	0.0155
Hydrogen chloride (ppmv)	50	50 ppmv or 90% removal	41.7
Sulfur dioxide‡ (ppmv)	50	Use HCl	22.9
Lead (lb/ton)	0.0005	Risk assessment	0.000011
Arsenic (lb/ton)	0.00001	Risk assessment	<0.000003
Mercury (lb/ton)	0.0015	Risk assessment	0.0006
Cadmium (lb/ton)	0.00002	Risk assessment	<0.000003
Carbon monoxide§ (ppmv)	50	Use combustion efficiency	46.2

gr/dscf = grains per dry standard cubic foot
ng/dscm = nanograms per dry standard cubic meter
ppmv = parts per million by volume
lb/ton = pounds per ton of refuse processed
*Concentrations are corrected to 12 percent CO_2 basis.
†PCDD/PCDF toxic equivalents as defined by NYSDEC.
‡8-hour average.
§4-hour average.
Data provided by Taconic Resources, Inc., Jan. 12, 1993. Inform Publication, *A Solid Waste Blueprint for New York State,* March 1988.

TABLE 25-71 Important Factors in Preliminary Selection of Landfill Sites

Factor	Remarks
Available land area	In selecting potential land disposal sites, it is important to ensure that sufficient land area is available. Sufficient area to operate for at least 1 year at a given site is needed to minimize costs.
Impact of processing and resource recovery	It is important to project the extent of resource-recovery-processing activities that are likely to occur in the future and determine their impact on the quantity and condition of the residual materials to be disposed of.
Haul distance	Although minimum haul distances are desirable, other factors must also be considered. These include collection-route location, types of wastes to be hauled, local traffic patterns, and characteristics of the routes to and from the disposal site (condition of the routes, traffic patterns, and access conditions).
Soil conditions and topography	Because it is necessary to provide material for each day's landfill and a final layer of cover after the filling has been completed, data on the amounts and characteristics of the soils in the area must be obtained. Local topography will affect the type of landfill operation to be used, equipment requirements, and the extent of work necessary to make the site usable.
Climatological conditions	Local weather conditions must also be considered in the evaluation of potential sites. Under winter conditions where freezing is severe, landfill cover material must be available in stockpiles when excavation is impractical. Wind and wind patterns must also be considered carefully. To avoid blowing or flying papers, windbreaks must be established.
Surface-water hydrology	The local surface-water hydrology of the area is important in establishing the existing natural drainage and runoff characteristics that must be considered. Other conditions of flooding must also be identified.
Geologic and hydrogeologic conditions	Geologic and hydrogeologic conditions are perhaps the most important factors in establishing the environmental suitability of the area for a landfill site. Data on these factors are required to assess the pollution potential of the proposed site and to establish what must be done to the site to control the movement of leachate or gases from the landfill.
Local environmental conditions	The proximity of both residential and industrial developments is extremely important. Great care must be taken in their operation if they are to be environmentally sound with respect to noise, odor, dust, flying paper, and vector control.
Ultimate uses	Because the ultimate use affects the design and operation of the landfill, this issue must be resolved before the layout and design of the landfill are started.

over the completed fill. The cover material must be hauled in by truck or earth-moving equipment from adjacent land or from borrow-pit areas. In some newer landfill operations, the daily cover material is omitted. A completed lift, including the cover material is called a "cell" (see Fig. 25-69). Successive lifts are placed on top of one another until the final grade called for in the ultimate development plan is reached. A final layer of cover material is used when the fill reaches the final design height.

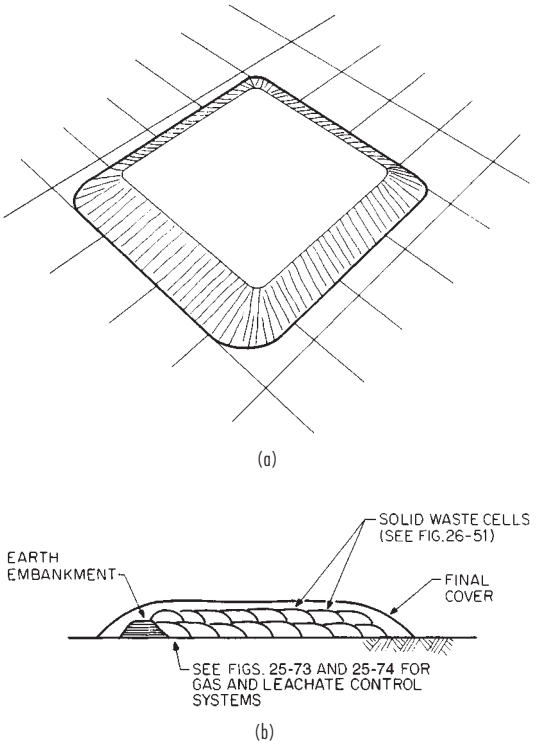


FIG. 25-68 Area method for landfilling solid wastes. (*a*) Pictorial view of completed landfill. (*b*) Section through landfill.

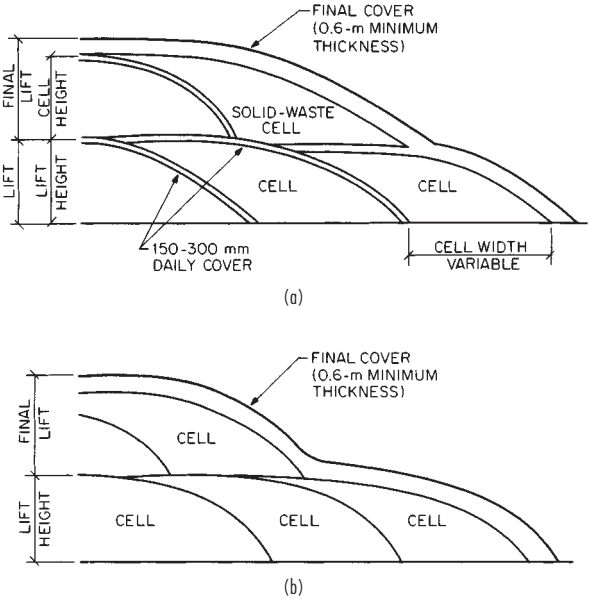


FIG. 25-69 Typical section through a landfill. (*a*) With daily or intermediate cover. (*b*) Without daily or intermediate cover.

2. *Depression method.* At locations where natural or artificial depressions exist, it is often possible to use them effectively for landfilling operations. Canyons, ravines, dry borrow pits, and quarries have been used for this purpose. The techniques to place and compact solid wastes in depression landfills vary with the geometry of the site, the characteristics of the cover material, the hydrology and geology of the site, and access of the site.

In a canyon site, filling starts at the head end of the canyon (see Fig. 25-70) and ends at the mouth. The practice prevents the accumulation of water behind the landfill. Wastes usually are deposited on the canyon floor and from there are pushed up against the canyon face at a slope of about 2 to 1. In this way, a high degree of compaction can be achieved.

3. *Landfills in wet areas.* Because of the problems associated with contamination of local groundwaters, the development of odors, and structural stability, landfills must be avoided in wetlands. If wet areas such as ponds, pits, or quarries must be used as landfill sites, special provisions must be made to contain or eliminate the movement of leachate and gases from completed cells. Usually this is accomplished by first draining the site and then lining the bottom with a clay liner or other appropriate sealants. If a clay liner is used, it is important to continue operation of the drainage facility until the site is filled to avoid the creation of uplift pressures that could cause the liner to rupture from heaving.

Occurrence of Gases and Leachate in Landfills The following biological, physical, and chemical events occur when solid wastes are placed in a sanitary landfill: (1) biological decay of organic materials, either aerobically or anaerobically, with the evolution of gases and liquids; (2) chemical oxidation of waste materials; (3) escape of gases from the fill; (4) movement of liquids caused by differential heads; (5) dissolving and leaching of organic and inorganic materials by water and leachate moving through the fill; (6) movement of dissolved material by concentration gradients and osmosis; and (7) uneven settlement caused by consolidation of material into voids.

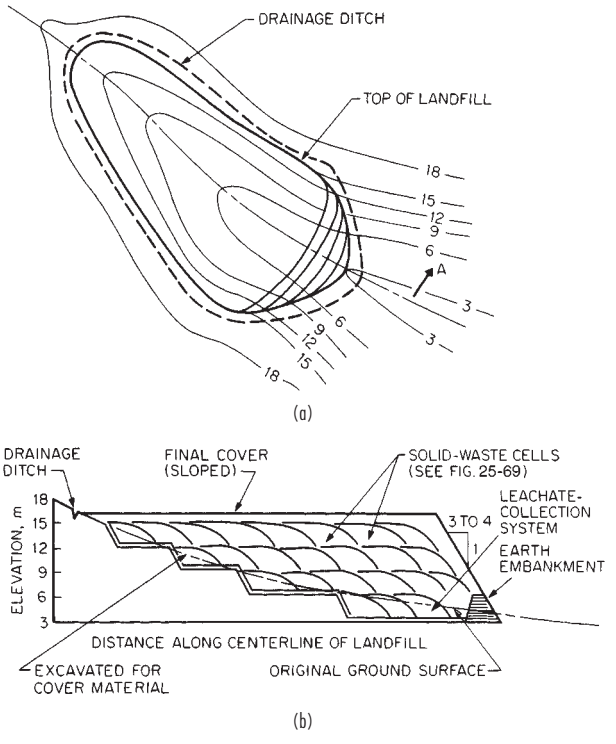


FIG. 25-70 Depression method for landfilling solid wastes. (*a*) Plan view: canyon-site landfill. (*b*) Section through landfill.

With respect to item 1, bacterial decomposition initially occurs under aerobic conditions because a certain amount of air is trapped within the landfill. However, the oxygen in the trapped air is exhausted within days, and long-term decomposition occurs under anaerobic conditions.

1. *Gases in landfills.* Gases found in landfills include air, ammonia, carbon dioxide, carbon monoxide, hydrogen, hydrogen sulfide, methane, nitrogen, and oxygen. Data on the molecular weight and density of these gases are presented in Sec. 2. Carbon dioxide and methane are the principal gases produced from the anaerobic decomposition of the organic solid-waste components.

The anaerobic conversion of organic compounds is thought to occur in three steps: The first involves the enzyme-mediated transformation (hydrolysis) of higher-weight molecular compounds into compounds suitable for use as a source of energy and cell carbon; the second is associated with the bacterial conversion of the compounds resulting from the first step into identifiable lower-molecular-weight intermediate compounds; and the third step involves the bacterial conversion of the intermediate compounds into simpler end products, such as carbon dioxide (CO_2) and methane (CH_4). The overall anaerobic conversion of organic industrial wastes can be represented with the following equation:

$$C_aH_bO_cN_d \rightarrow nC_wH_xO_yN_z + mCH_4 + sCO_2 + rH_2O + (d - nz)NH_3 \quad (25\text{-}26)$$

where $s = a - nw - m$
$r = c - ny - 2s$

The terms $C_aH_bO_cN_d$ and $C_wH_xO_yN_z$ are used to represent on a molar basis the composition of the material present at the start of the process. If it is assumed that the organic wastes are stabilized completely, the corresponding expression is

$$C_aH_bO_cN_d + \left(\frac{4a - b - 2c + 3d}{4}\right)H_2O \rightarrow \left(\frac{4a + b - 2c - 3d}{8}\right)CH_4 + \left(\frac{4a - b + 2c + 3d}{8}\right)CO_2 + dNH_3 \quad (25\text{-}27)$$

The rate of decomposition in unmanaged landfills, as measured by gas production, reaches a peak within the first 2 years and then slowly tapers off, continuing in many cases for periods up to 25 years or more. The total volume of the gases released during anaerobic decomposition can be estimated in a number of ways. If all the organic constituents in the wastes (with the exception of plastics, rubber, and leather) are represented with a generalized formula of the form $C_aH_bO_cN_d$, the total volume of gas can be estimated by using Eq. (25-27) with the assumption of completed conversion to carbon dioxide and methane.

2. *Leachate in landfills.* Leachate may be defined as liquid that has percolated through solid waste and has extracted dissolved or suspended materials from it. In most landfills, the liquid portion of the leachate is composed of the liquid produced from the decomposition of the wastes and liquid that has entered the landfill from external sources, such as surface drainage, rainfall, groundwater, and water form underground springs. Representative data on chemical characteristics of leachate are reported in Table 25-72.

Gas and Leachate Movement and Control Under ideal conditions, the gases generated from a landfill should be either vented to the atmosphere or, in larger landfills, collected for the production of energy. Landfills with >2.5 million cubic meters of waste or >50 Mg/y NMOC (nonmethane organic compounds) emissions may require landfill-gas collection and flare systems, per EPA support WWW, CFR 60 Regulations. The leachate should be either contained within the landfill or removed for treatment.

1. *Gas movement.* In most cases, over 90 percent of the gas volume produced from the decomposition of solid wastes consists of methane and carbon dioxide. Although most of the methane escapes to the atmosphere, both methane and carbon dioxide have been found in concentrations of up to 40 percent at lateral distances of up to 120 m (400 ft) from the edges of landfills. Methane can accumulate below buildings or in other enclosed spaces on or close to a sanitary landfill. With proper venting, methane should not pose a problem.

TABLE 25-72 Typical Leachate Quality of Municipal Waste

S1 Number	Parameter	Overall range (mg/liter except as indicated)
1	TDS	584–55,000
2	Specific conductance	480–72,500 u.mho/cm
3	Total suspended solids	2–140,900
4	BOD	ND–195,000
5	COD	6.6–99,000
6	TOC	ND–40,000
7	pH	3.7–8.9 units
8	Total alkalinity	ND–15,050
9	Hardness	0.1–225,000
10	Chloride	2–11,375
11	Calcium	3.0–2,500
12	Sodium	12–6,010
13	Total Kjeldahl nitrogen	2–3,320
14	Iron	ND–4,000
15	Potassium	ND–3,200
16	Magnesium	4.0–780
17	Ammonia-nitrogen	ND–1,200
18	Sulfate	ND–1,850
19	Aluminum	ND–85
20	Zinc	ND–731
21	Manganese	ND–400
22	Total phosphorus	ND–234
23	Boron	0.87–13
24	Barium	ND–12.5
25	Nickel	ND–7.5
26	Nitrate-nitrogen	ND–250
27	Lead	ND–14.2
28	Chromium	ND–5.6
29	Antimony	ND–3.19
30	Copper	ND–9.0
31	Thallium	ND–0.78
32	Cyanide	ND–6
33	Arsenic	ND–70.2
34	Molybdenum	0.01–1.43
35	Tin	ND–0.16
36	Nitrite-nitrogen	ND–1.46
37	Selenium	ND–1.85
38	Cadmium	ND–0.4
39	Silver	ND–1.96
40	Beryllium	ND–0.36
41	Mercury	ND–3.0
42	Turbidity	40–500 Jackson units

From McGinely, P. M. and Kmet, P., *Formation Characteristics, Treatment, and Disposal of Leachate from Municipal Solid Waste Landfills,* Bureau of Solid Waste Management, Wisconsin Department of Natural Resources, Madison, 1984.

Because carbon dioxide is about 1.5 times as dense as air and 2.8 times as dense as methane, it tends to move toward the bottom of the landfill. As a result, the concentration of carbon dioxide in the lower portions of landfill may be high for years. Ultimately, because of its density, carbon dioxide will also move downward through the underlying formation until it reaches the groundwater. Because carbon dioxide is readily soluble in water, it usually lowers the pH, which in turn can increase the hardness and mineral content of the groundwater through the solubilization of calcium and magnesium carbonates.

2. *Control of gas movement.* The lateral movement of gases produced in a landfill can be controlled by installing vents made of materials that are more permeable than the surrounding soil. Typically, as shown in Fig. 25-71*a,* gas vents are constructed of gravel. The spacing of cell vents depends on the width of the waste cell but usually varies from 18 to 60 m (60 to 200 ft). The thickness of the gravel layer should be such that it will remain continuous even though there may be differential settling; 300 to 450 mm (12 to 18 in) is recommended. Barrier vents (see Fig. 25-71*b*) also can be used to control the lateral movement of gases. Well vents are often used in conjunction with lateral surface vents buried below grade in a gravel trench (see Fig. 25-71*c*). Details of a gas vent are shown in Fig. 25-72. Control of the downward movement of gases can be accomplished by installing perforated pipes in the gravel layer at the bottom of the landfill. If the gases cannot be vented laterally, it may be necessary to install gas wells

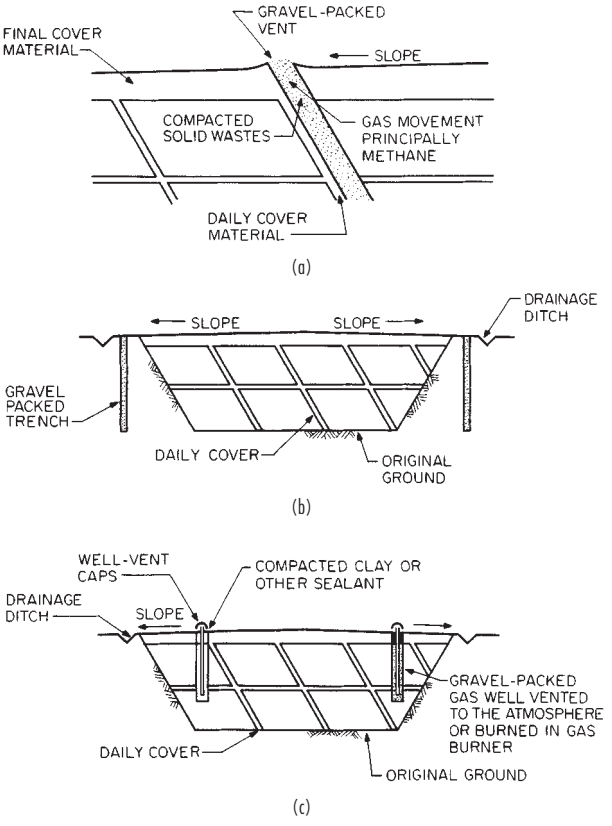


FIG. 25-71 Vents used to control the lateral movement of gases in landfills. (*a*) Cell. (*b*) Barrier. (*c*) Well. (*From G. Tchobanoglous, H. Theisen, and R. Eliassen,* Solid Wastes: Engineering Principles and Management Issues, *McGraw-Hill, New York, 1977.*)

and vent the gas to the atmosphere. This is considered a passive venting system. See Fig. 25-73.

The movement of landfill gases through adjacent soil formations can be controlled by constructing barriers of materials that are more impermeable than the soil (see Fig. 25-74*a*). Some of the landfill

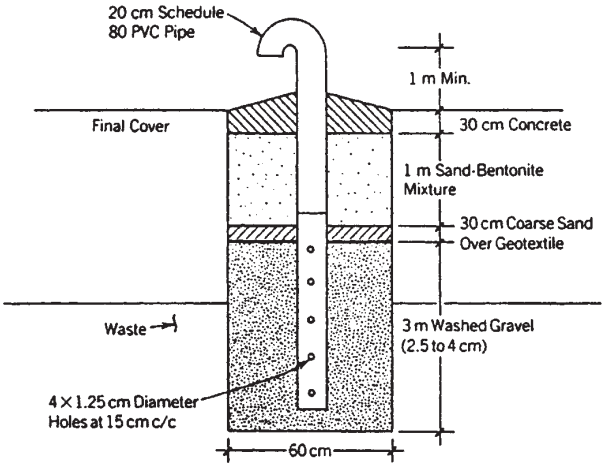


FIG. 25-72 Typical detail of an isolated gas vent. (*From Bagchi, A.,* Design, Construction, and Monitoring of Sanitary Landfill, *Wiley, 1990.*)

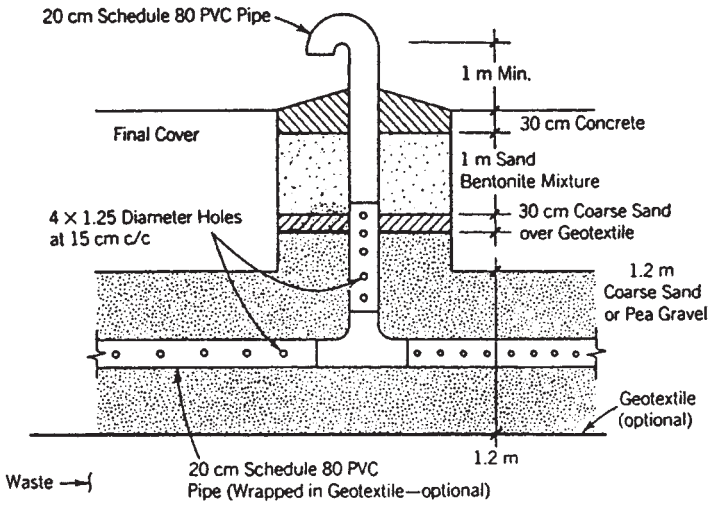


FIG. 25-73 Typical detail of a passive gas venting system with a header pipe. (*From Bagchi, A.*, Design, Construction, and Monitoring of Sanitary Landfill, *Wiley, 1990.*)

sealants that are available for this use are identified in Table 25-73. Of these, the use of compacted clays is the most common. The thickness will vary depending on the type of clay and the degree of control required; thickness ranging from 0.15 to 1.25 m (6 to 48 in) have been used. Covers of landfills are also typically multi-layer-foundation layer, clay layer, membrane, drainage layer (synthetic or natural) root zone layer, or soil.

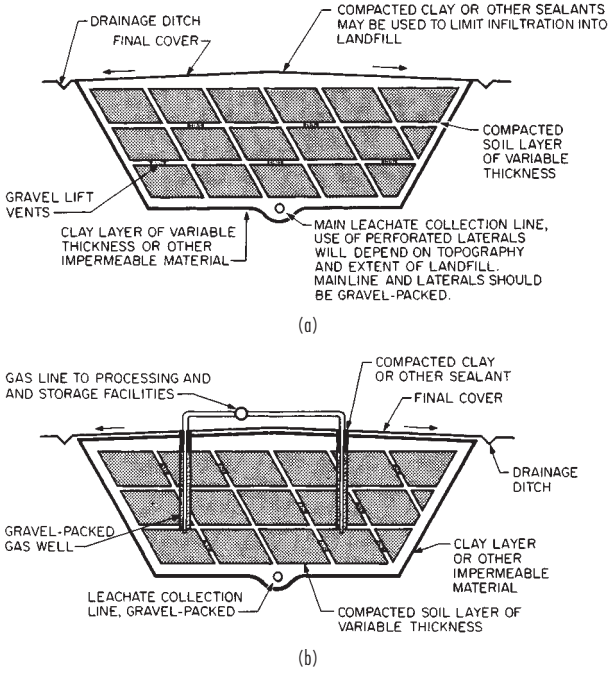


FIG. 25-74 Use of an impermeable liner to control the movement of gases and leachate in landfills. (*a*) Without gas recovery. (*b*) With gas recovery. (*From G. Tchobanoglous, H. Theisen, and R. Eliassen,* Solid Wastes: Engineering Principles and Management Issues, *McGraw-Hill, New York, 1977.*)

3. *Control of gas movement by recovery.* The movement of gases in landfills can also be controlled by installing gas-recovery wells in completed landfills (see Fig. 25-74*b*). This is considered an active venting system. Clay and other liners are used when landfill gas is to be recovered. In some gas-recovery systems, leachate is collected and recycled to the top of the landfill and reinjected through perforated lines located in drainage trenches. Typically, the rate of gas production is greater in leachate-recirculation systems.

Gas-recovery systems have been installed in some large municipal landfills. The economics of such operations must be reviewed for each

TABLE 25-73 Landfill Sealants for the Control of Gas and Leachate Movement

Sealant		
Classification	Representative types	Remarks
Compacted soil		Should contain some clay or fine silt.
Compacted clay	Bentonites, illites, kaolinites	Most commonly used sealant for landfills; layer thickness varies from 0.15–1.25 m; layer must be continuous and not be allowed to dry out and crack.
Inorganic chemicals	Sodium carbonate, silicate, or pyrophosphate	Use depends on local soil characteristics.
Synthetic chemicals	Polymers, rubber latex	Experimental; use not well established.
Synthetic membrane liners	Polyvinyl chloride, butyl rubber, Hypalon, polyethylene, nylon-reinforced liners	Expensive; may be justified where gas is to be recovered.
Asphalt	Modified asphalt, asphalt-covered polypropylene fabric, asphalt concrete	Layer must be thick enough to maintain continuity under differential settling conditions.
Others	Gunite concrete, soil cement, plastic soil cement	

°From G. Tchobanoglous, H. Theisen, and R. Eliassen, *Solid Wastes: Engineering Principles and Management Issues*, McGraw-Hill, New York, 1977.

site. The end use of gas will affect the overall economics. The cost of gas-cleanup and -processing equipment will limit the recovery of landfill gases, especially from small landfills.

4. *Leachate movement.* Under normal conditions, leachate is found in the bottom of landfills. From there it moves through the underlying strata, although some lateral movement may also occur, depending on the characteristics of the surrounding material. The rate of seepage of leachate from the bottom of a landfill can be estimated by Darcy's law by assuming that the material below the landfill to the top of the water table is saturated and that a small layer of leachate exists at the bottom of the fill. Under these conditions, the leachate discharge rate per unit area is equal to the value of the coefficient of permeability *K*, expressed in meters per day. The computed value represents the maximum amount of seepage that would be expected, and this value should be used for design purposes. Under normal conditions, the actual rate would be less than this value because the soil column below the landfill would not be saturated. Models have been developed to aid in the estimation of leachate quantity. Bagchi has covered details of these models in the *Design, Construction, and Monitoring of Sanitary Landfill.*

5. *Control of leachate movement.* As Leachate percolates through the underlying strata, many of the chemical and biological constituents originally contained in it will be removed by the filtering and adsorptive action of the material composing the strata. In general, the extent of this action depends on the characteristics of the soil, especially the clay content. Because of the potential risk involved in allowing leachate to percolate to the groundwater, best practice calls for its elimination or containment. Ultimately, it will be necessary to collect and treat the leachate.

The use of clay has been the favored method of reducing or eliminating the percolation of leachate (see Fig. 25-74 and Table 25-73). Membrane liners are used most often today but require care so that they will not be damaged during the filling operations. Equally important in controlling the movement of leachate is the elimination of surface-water infiltration, which is the major contributor to the total volume of leachate. With the use of an impermeable clay layer, membrane liners, an appropriate surface slope (1 to 2 percent), and adequate drainage, surface infiltration can be controlled effectively.

6. *Settlement and structural characteristics of landfills.* The settlement of landfills depends on the initial compaction, characteristics of wastes, degree of decomposition, and effects of consolidation when the leachate and gases are formed in the landfill. The height of the completed fill will also influence the initial compaction and degree of consolidation.

Design and Operation of Landfills Important design considerations in the design and operation of landfills include (1) land requirements, (2) types of wastes that must be handled, (3) evaluation of seepage potential, (4) design of drainage and seepage-control facilities, (5) development of a general operation plan, (6) design of solid-waste-filling plan, and (7) determination of equipment requirements. The more important individual factors that must be considered in the design of a landfill are reported in Table 25-74. The last three items are considered further in the following discussion.

1. *Landfill-operation plan.* The layout of the site and the development of a workable operating schedule are the main features of a landfill-operation plan. In planning the layout of a landfill site, the location of the following must be determined: (1) access roads; (2) equipment shelters; (3) scales, if used; (4) storage sites for special wastes; (5) topsoil-stockpile sites; (6) landfill areas; and (7) plantings.

2. *Solid-waste-filling plan.* The specific method of filling will depend on the characteristics of the site, such as the amount of available cover material, the topography, and local hydrology and geology. To assess future development plans, it will be necessary to prepare a detailed plan for the layout of the individual solid-waste cells. On the basis of the characteristics of the site or the method of operation (e.g., gas recovery), it may be necessary to incorporate special features for the control of the movement of gases and leachate from the landfill.

3. *Equipment requirements.* The types of equipment that have been used at sanitary landfills include both crawler and rubber-tired tractors, scrapers, compactors, draglines, and graders. The size and amount of equipment required will depend primarily on local site

TABLE 25-74 Important Factors That Must Be Considered in Design and Operation of Solid-Waste Landfills

Factor	Remarks	Factor	Remarks
Design		Landfilling method	Selection of method will vary with terrain and available cover.
Access	Paved all-weather access roads to landfill site; temporary roads to unloading areas.	Litter control	Use movable fences at unloading areas; crews should pick up litter at least once per month or as required.
Cell design and construction	Will vary depending on terrain, landfilling method, and whether gas is to be recovered.	Operation plan	With or without the codisposal of treatment-plant sludges and the recovery of gas.
Cover material	Maximize use of on-site earth materials; approximately 1 m^3 of cover material will be required for every 4 to 6 m^3 of solid wastes; mix with sealants to control surface infiltration. In some designs, intermediate cover is not used.	Spread and compaction	Spread and compact waste in 0.6-m (2-ft) layers.
		Unloading area	Keep small, generally under 30 m (100 ft).
Drainage	Install drainage ditches to divert surface-water runoff; maintain 1 to 2 percent grade on finished fill to prevent ponding. TCLP Tests	Operation	
		Communications	Telephone for emergencies.
		Days and hours of operation	Usual practice is 5 to 6 days/week and 8 to 10 h/day.
Equipment requirements	Vary with size of landfills.	Employee facilities	Rest rooms and drinking water should be provided.
Fire prevention	Water on site; if nonpotable, outlets must be marked clearly; proper cell separation prevents continuous burn-through if combustion occurs.	Equipment maintenance	A covered shed should be provided for field maintenance of equipment.
Groundwater protection	Divert any underground springs; if required, install sealants for leachate control; install wells for gas and groundwater monitoring.	Operational records	Tonnage, transactions, and billing if a disposal fee is charged.
		Salvage	No scavenging; salvage should occur away from the unloading area; no salvage storage on site.
Land area	Area should be large enough to hold all wastes for a minimum of 5 years but preferably for 25 to 30 years.	Scales	Essential for record keeping.

conditions, the size of the landfill operation, and the method of operation.

Landfilling of Hazardous Wastes In many states, the only disposal option available for most hazardous wastes is landfilling. The basis for the management of hazardous-wastes landfills is set forth in the Resource Conservation and Recovery Act of 1976. In general, disposal sites for hazardous wastes should be separate from sites for municipal solid wastes. If separate sites are not possible, great care must be taken to ensure that separate disposal operations are maintained.

Requirements The requirements for a hazardous-waste landfill are detailed in RCRA and the regulations developed to implement the act. From a design standpoint, two of the most important requirements are (1) complete leachate containment, and (2) control of the surface water on and around the site.

Site Selection Factors that must be considered in evaluating potential sites for the disposal of hazardous waste are covered in state and federal regulations. In California, landfills where hazardous wastes can be received are referred to as Class I disposal sites. To qualify as a Class I site, it must be shown that:

1. Geological conditions are naturally capable of preventing vertical hydraulic continuity between liquids and gases emanating from the waste in the site and usable surface or groundwaters.
2. Geological conditions are naturally capable of preventing lateral hydraulic continuity between liquids and gases emanating from wastes in the site and usable surface or groundwaters, or the disposal area has been modified to achieve such capability.
3. Underlying geological formations that contain rock fractures or fissures of questionable permeability must be permanently sealed to provide a competent barrier to the movement of liquids or gases from the disposal site to usable water.
4. Inundation of disposal areas shall not occur until the site is closed in accordance with requirements of the regional board.
5. Disposal areas shall not be subject to washout.
6. Leachate and subsurface flow into the disposal areas shall be contained within the site unless other disposition is made in accordance with requirements of the regional board.
7. Site shall not be located over zones of active faulting or where other forms of geological change would impair the competence of natural features or artificial barriers which prevent continuity with usable waters.
8. Sites made suitable for use by human-made physical barriers shall not be located where improper operations or maintenance of such structures could permit the waste, leachate, or gases to contact usable groundwater of surface water.
9. Sites that comply with the above-noted clauses but would be subject to inundation by a tide or a flood of greater than 100-year frequency may be considered by the regional board as limited Class I disposal sites.

Landfilling Methods and Operations Operation of a landfill for hazardous wastes is quite different from that of a conventional landfill.

Many but not all hazardous wastes can be disposed of on land in properly designed landfills. To minimize potentially adverse environmental effects from wastes deposited at hazardous-waste landfill sites, the U.S. Environmental Protection Agency (EPA) has developed specific regulations regarding the characteristics of wastes suitable for landfilling. These regulations (40 CFR 265) include a prohibition on the placement of:

- Noncontainerized hazardous wastes containing free liquids, whether or not adsorbents have been added.
- Containers holding free liquids unless all freestanding liquid has been removed by decanting or other methods or has been mixed with absorbent or solidified so that freestanding liquid is no longer observed. Such containers must be at least 90 percent full or, if empty, reduced in size as much as possible via crushing or shredding prior to disposal.

The following containers are exempt from the above regulations:

- Very small containers, such as ampules, and containers holding liquids for use other than storage, such as batteries, which may be disposed directly in a hazardous-waste landfill.
- Small lab-pack containers of hazardous waste if they are first placed in nonleaking, larger containers. These containers must be filled to capacity and surrounded by enough absorbent material to contain the liquid contents of the lab pack. The resultant container must then be placed in a larger container packed with absorbent material which will not react with, become decomposed by, or ignited by the contents of the inside containers. Incompatible wastes may not be packed and disposed of together in this manner.

Design of Hazardous-Waste Landfills Most of the regulations governing the design of hazardous-waste landfills have been resolved. Although specific requirements will vary, the factors identified in Table 25-74 can be used as a design guide. Some special precautions that can be taken to prevent contamination of underlying strata are shown in Figs. 25-75 to 25-77. Figures 25-76 and 25-77 illustrate a conceptual design for a typical control-cell grid system for a hazardous waste landfill.

Landfarming Landfarming is a waste-disposal method in which the biological, chemical, and physical processes that occur in the surface of the soil are used to treat biodegradable industrial wastes. Wastes to be treated are either applied on top of the land which has

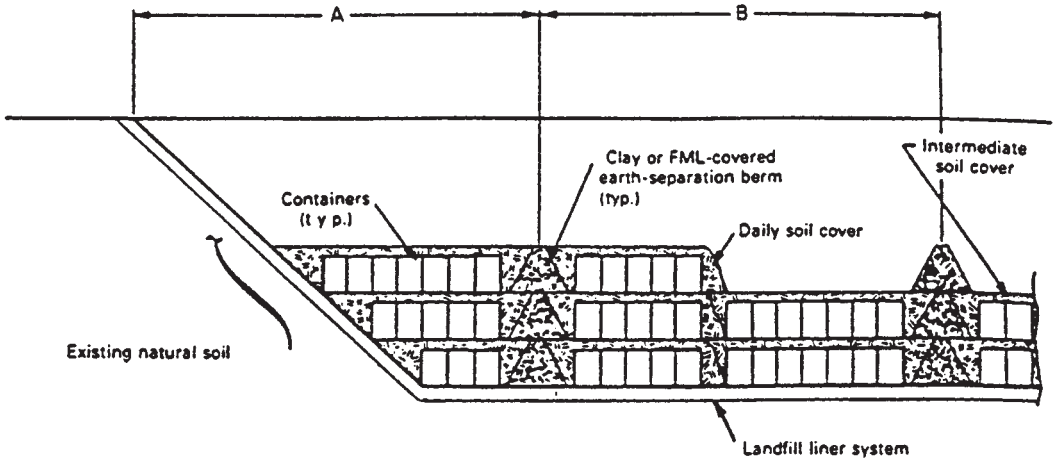


FIG. 25-75 Conceptual design for control cells for hazardous-waste disposal (section view). FML = flexible-membrane liner. (*From Freeman, H. M.,* Standard Handbook of Hazardous Waste Treatment and Disposal, *McGraw-Hill, 1988.*)

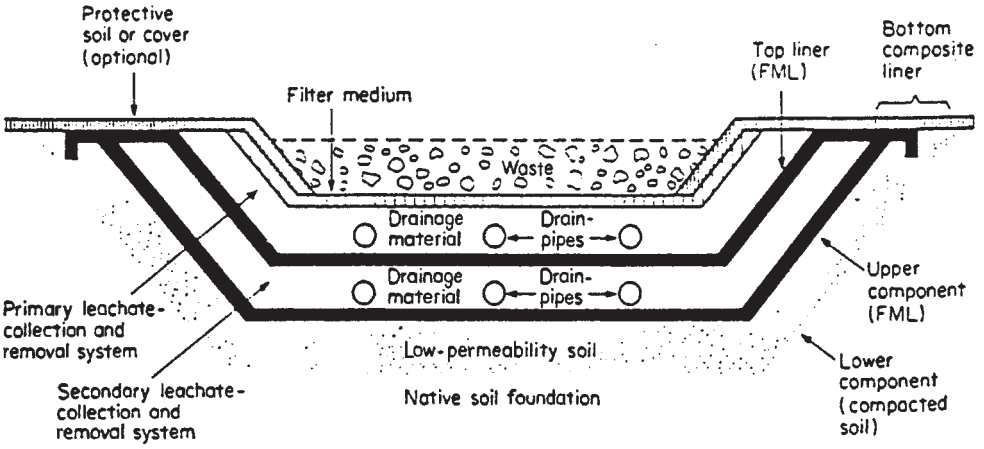


FIG. 25-76 Schematic of an FML plus compacted-soil double-liner system for a landfill. (Drawing not to scale.) (*U.S. EPA, EPA/530/SW-85-012. Washington, D.C., 1985. From Freeman, H. M.,* Standard Handbook of Hazardous Waste Treatment and Disposal, *McGraw-Hill, 1988.*)

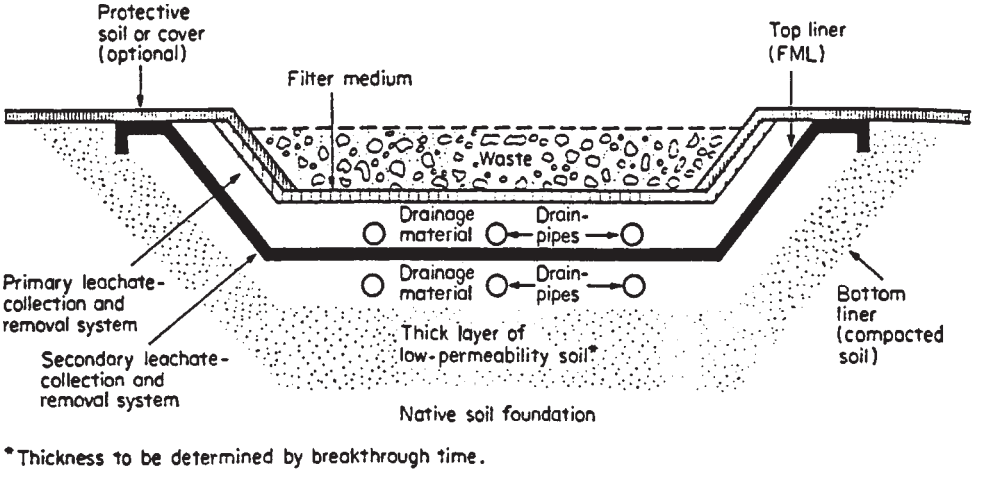


FIG. 25-77 Schematic of an FML plus composite double-liner system for a landfill. (Drawing not to scale.) (*U.S. EPA, EPA/530/SW-85-012, Washington, D.C., 1985. From Freeman, H. M.,* Standard Handbook of Hazardous Waste Treatment and Disposal, *McGraw-Hill, 1988.*)

been prepared to receive the wastes or injected below the surface of the soil.

Process Description When organic wastes are added to the soil, they are subjected simultaneously to the following processes: (1) bacterial and chemical decomposition, (2) leachating of water-soluble components in the original wastes and from the decomposition products, and (3) volatilization of selected components in the original wastes and from the products of decomposition.

Factors that must be considered in evaluating the biodegradability of organic wastes in a landfilling application include (1) composition of the waste; (2) compatibility of wastes and soil microflora; (3) environmental requirements including oxygen, temperature, pH, and inorganic nutrients; and (4) moisture content of soil-waste mixture.

Although most of the volatile components are released to the atmosphere, a small fraction is dissolved and/or carried away with the water in the soil matrix. Leached waters are carried with the water as it percolates through the underlying soil strata. Most of the organic constituents contained in the leachate receive additional treatment as they pass through the soil column. Leached wastes can also be lost in surface runoff.

Applications Landfarming is suitable for wastes that contain organic constituents that are biodegradable and are not subject to significant leaching while the bioconversion process is occurring. For example, petroleum oily wastes and oily sludges are ideally suited for disposal by landfarming. A variety of other organic wastes with similar characteristics are also suitable. Properly managed landfarming sites can be reused at frequent intervals with no adverse effects.

Design and Operation Important consideration in the design and operation of landfarming systems include (1) site selection, (2) site preparation, (3) waste characteristics, (4) method of waste application, (5) waste-application rate, (6) site management, and (7) monitoring. Important factors related to these design and operation considerations are reported in Table 25-75.

Deep-Well Injection Deep-well injection for the disposal of liquid wastes involves injecting the wastes deep in the ground into permeable rock formation (typically limestone or dolomite) or underground caverns.

Process Description The installation of deep wells for the injection of wastes closely follows the practices used for the drilling and completion of oil and gas wells.

TABLE 25-75 Important Design and Operation Considerations for Landfarming Systems Used for Waste Treatment

Item	Remarks
Site selection location	Proximity to critical areas specified in government regulations, accessibility, site geology and hydrology.
Site selection: soil characteristics	Adequate area soil cover and depth to groundwater usually greater than 1.5 m (4 ft). Slope should not exceed 5 to 8 percent. Soil type, including ion-exchange capacity.
Site preparation	Area should be fenced, graded for runoff control, and disked or plowed before waste application.
Waste characterization	Suspended solids, organic content, nitrogen (all forms), phosphorus pH, and inorganic metals including arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, silver, sodium, and zinc.
Method of waste application	Ridge and furrow, sprinkling (fixed or portable systems), tank-truck spreading, subsurface injection.
Waste-application rates	For petroleum crude oil and lubricating oils the range is from 250 to 1250 bbl/(ha · year) with a value of 400 bbl/(ha · year) being typical. A typical value for general refinery oils and wastes would be about 150 bbl/(ha · year).
Site management	Wastes spread on the surface should be disked or plowed into the soil soon after application (1 to 7 days). To promote aerobic conditions and rapid bioconversion of the wastes the soil-waste mixture should be cultivated periodically.
Monitoring	Periodic samples should be taken to assess the extent of completion of the bioconversion process. Core samples should be taken annually to monitor the movement of leached wastes in the underlying strata.

Examination of the records of wastewater injection wells that have been constructed in the United States shows that almost all the wells constructed thus far have been completed by one of three methods or close variations of them. The methods are:

1. Open-hole completion in competent formations
2. Screened or screened and gravel-packed in incompetent sands and gravels
3. Fully cased and cemented with the casing perforated in either competent or somewhat incompetent formations

Most wastewater injection wells will be constructed with injection

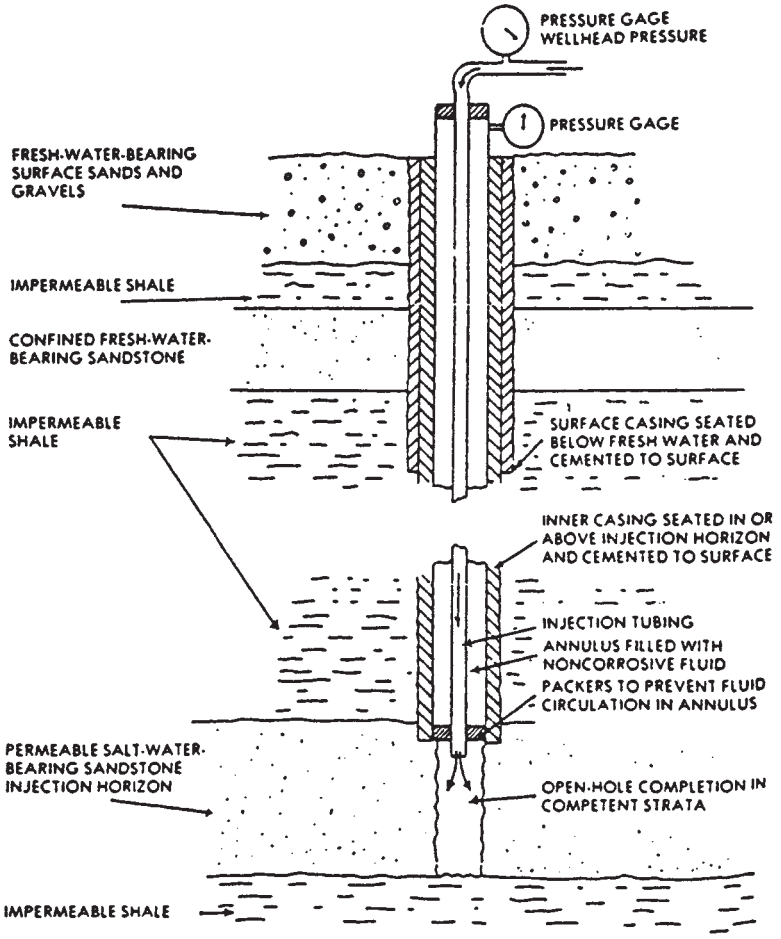


FIG. 25-78 Schematic diagram of an industrial-waste injection well completed in competent sandstone. (*From Freeman, H. M.,* Standard Handbook of Hazardous Waste Treatment and Disposal, *McGraw-Hill, 1988.*)

TABLE 25-76 Important Design and Operation Considerations for Deep Wells Used for Waste Injection

Item	Remarks	Item	Remarks
Well-site selection	Criteria for assessing the feasibility of a deep-well-injection site include (1) uniformity, (2) large extent, (3) substantial thickness, (4) high porosity and permeability, (5) low pressure, (6) saline aquifer, (7) separation from potable-water horizons, (8) adequate overlying and underlying aquicludes, (9) no poorly plugged wells nearby, and (10) compatibility between the mineralogy and fluids of the reservoir and the injected wastes.		injection formation). Adjustment of pH and buffering of the waste may be necessary.
		Deep-well installation	Well depths vary from 550 to 3660 m (1800 to 1200 ft); well-injection rates vary from 4 to 60 L/s; rates in the range from 15 to 20 L/s are typical. Operation pressures up to 27,600 kPa (4000 psig) are used.
		Monitoring	Continuous monitoring facilities should be installed when wells are put into operation. Irregularities in the pressure may require changes in operating procedures.
Waste pretreatment	Suspended solid less than 10 to 15 mg/L; particle sizes equal to or less than 1 to 5 μm (depends on		

tubing inside the long casing string, and with a packer set between the tubing and the casing near the bottom of the casing (Fig. 25-78). This design is not entirely free of problems, particularly with the packer, but experience has proved it generally superior to other designs. Some wells are completed with an annulus open at the bottom. The annulus is filled with a lighter-than-waste liquid that "floats" on the aqueous waste. This type of well completion has been referred to as a *fluid-seal completion.*

Applications Deep-well injection has been used principally for liquid wastes that are difficult to treat and dispose of by more conventional methods and for hazardous wastes. Chemical, petrochemical, and pharmaceutical wastes are those most commonly disposed of with this method. The waste may be liquid, gases, or solids. The gases and solids are either dissolved in the liquid or are carried along with the liquid.

Design and Operation Important design and operation considerations for deep-well injection are related to (1) well-site selection, (2) pretreatment, (3) installation of an injection well, and (4) monitoring. Important factors related to these design and operation considerations are reported in Table 25-76. As noted in the table, wastes are usually treated prior to injection to prevent clogging of the formation and damage to equipment. Particles greater than about 1 to 5 μm must be removed. Typically, treated wastes must be filtered prior to injection. Wastes must also be compatible with the characteristics of the aquifer. This may require pH adjustment and the use of compatible buffers.

Ocean Disposal of Solid Wastes Although ocean dumping of municipal solid wastes was abandoned in the United States in 1933, the concept has persisted throughout the years and is still frequently discussed today. Some industrial wastes are still discharged at sea. Within the past few years, the idea that the ocean is a gigantic sink, into which an infinite amount of pollution of all types can be dumped, has been discarded. On the other hand, it is argued that many of the wastes now placed in landfills or on land could be used as fertilizers to increase the productivity of the ocean. It is also argued that the placement of wastes in ocean-bottom trenches where tectonic folding is occurring is an effective method of waste disposal.

PLANNING

Because of the ever-growing number of federal regulations governing the disposal of nonhazardous and hazardous solid wastes, it is prudent to develop both short-term and long-term action programs to deal with all aspects of solid-waste management. Important short- and long-term actions are identified in Table 25-77.

TABLE 25-77 Short- and Long-Term Actions for Effective Industrial Solid-Waste Management*

Actions	Remarks	Actions	Remarks
Short-term		Long-term	
1. Inventory wastes.	Document all types, quantities, and sources of wastes (both nonhazardous and hazardous wastes).	1. Remove all accumulated wastes.	Develop a systematic program for removing all accumulated wastes stored on the plant site.
2. Inventory inactive sites.	All inactive sites where wastes have been disposed of in the past should be inventoried. Data should be gathered on buried wastes, including types, quantity, and sources. A groundwater-monitoring program should be developed.	2. Separate wastes.	Institute a long-term program to separate wastes at the source of production.
		3. Reduce wastes.	A systematic program should be undertaken to examine all sources of waste production and to develop alternative operations and processes to reduce waste generation.
3. Characterize wastes.	In addition to general information on the characteristics of the wastes, all hazardous wastes should be individually characterized.	4. Improve facilities.	Upgrade facilities to meet RCRA requirements. A data-collection program should be instituted to obtain any needed data.
4. Assign responsibilities.	Assign responsibilities and authority at plant and headquarters for the storage, collection, treatment, and disposal of all types of hazardous wastes.	5. Review all waste-management agreements.	Develop detailed contracts with outside waste-management firms. Define clearly the duties and responsibilities of plant personnel and waste-collection personnel.
5. Track the movement of wastes.	Develop a logging system for hazardous wastes containing the date, waste description, source, volume shipped or hauled, name of hauler, and destination. Follow through to be sure that wastes reach destination.	6. Review and develop disposal-site options.	Develop long-term projections for landfill requirements and initiate a program to secure the needed sites.
		7. Secure appropriate engineering and consulting services.	Make sure that your engineering departments are involved early in the process. Retain outside consultants for specific tasks.
6. Develop emergency procedures.	Develop procedures for dealing with with emergency situations involving the storage, collection, treatment, and disposal of hazardous wastes.	8. Monitor legislative programs.	Develop a program for monitoring new regulations and for inputting to appropriate federal, state, and local agencies on the modification and development of new regulations.
7. Obtain permits.	Start obtaining the necessary waste-disposal permits as soon as possible.		

*Adapted in part from R. Sobel, "How Industry Can Prepare for RCRA," *Chem. Eng.,* **86**(1), 82 (Jan. 29, 1979).

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Section 26

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PROCESS SAFETY INTRODUCTION

In recent years there has been an increased emphasis on process safety as a result of a number of serious accidents. This is due in part to the worldwide attention to issues in the chemical industry brought on by several dramatic accidents involving gas releases, major explosions, and environmental incidents. Public awareness of these and other accidents has provided a driving force for industry to improve its safety record. Local and national governments are taking a hard look at safety in industry as a whole and the chemical industry in particular. There has been an increasing amount of government regulation.

The Chemical Process Industries constitutes one of the safest of the manufacturing sectors, but a single major accident or disaster can do irreparable damage to a company's reputation and possibly affect the entire industry (Sheridan, "OSHA, EPA and Process Sampling," *Chem. Proc.,* September 1994, pp. 24–28). One reason the chemical industry gets bad press is that its activities are very noticeable. Large chemical works are striking features on the landscape. Chemical plants are often noisy and garishly lit, and many of the effluents cause nuisances which are well below the health and safety limits. Hazardous chemicals are transported in bulk in highly visible container vehicles, adding to the public's image of the industry as hazardous and dangerous (Benson and Ponton, "Process Miniaturisation—A Route to Total Environmental Acceptability," *Institution of Chemical Engineers* 0263-8762/93). For many reasons, the public often associates the chemical industry with environmental and safety problems and, unfortunately, sometimes the negative image that goes with the problems is deserved. It is vital to the future of the chemical industry that process safety have a high priority in the design and operation of chemical process facilities.

Environmental pressures on the process industries will prove to be the most significant change for the next 50 years. Not only will new processes change, but mature industries will have to develop new process technology to survive (Benson et al., op. cit.).

Hazards from combustion and runaway reactions play a leading role in many chemical process accidents. Knowledge of these reactions is essential for control of process hazards. It is important that loss of containment be avoided. For example:

- Much of the damage and loss of life in chemical accidents results from the sudden release of material at high pressures which may or may not result from fire. Chemical releases caused by fires and the failure of process equipment and pipelines can form toxic clouds that can be dangerous to people over large areas.
- Vapor cloud explosions can result if clouds of flammable vapor in air are formed. It is important to understand how liquids and gases flow through holes in equipment and how resulting vapor or gas clouds are dispersed in air.
- Understanding how sudden pressure releases can occur is important. They can happen, for example, from ruptured high-pressure tanks, runaway reactions, flammable vapor clouds, or pressure developed from external fire. The proper design of pressure relief systems can reduce the possibility of losses from unintended overpressure.
- Static electricity is often a hidden cause in accidents.
- It is important to understand the reactive nature of the chemicals involved in a chemical facility.
- Loss of containment due to mechanical failure or misoperation is a major cause of chemical process accidents. The publication, *One Hundred Largest Losses: A Thirty Year Review of Property Damage Losses in the Hydrocarbon Chemical Industry,* 9th ed. (M&M Protection Consultants, Chicago), cites loss of containment as the leading cause of property loss in the chemical process industries.

Government regulations require hazard and risk analysis as part of *process safety management* (PSM) programs. These are part of the process safety programs of many chemical process facilities.

Process safety includes many subjects that could not be included in this section because of lack of space. The following describes the organization of Section 26:

Inherently Safer Design Rather than add on equipment to control hazards or to protect people from their consequences, it is better to design user-friendly plants which can withstand human error and equipment failure without serious effects on safety, the environment, output, and efficiency. This part is concerned with this matter.

Process Safety Analysis This part treats the analysis of a process or project from the standpoint of hazards, risks, procedures for making potential damage estimates, and project reviews and audits. It can be helpful to management in assessing risks in a project. It consists of the following:

Hazard Analysis
Risk Analysis
Guidelines for Estimating Damage
Project Reviews and Procedures

Safety Devices Pressure relief devices, flame arresters, and methods for handling effluent from controlled releases provide control of accidental undesirable events. Special equipment should be considered for highly toxic chemical service. The following matters are considered:

Pressure Relief Systems
Emergency Relief Device Effluent Collection and Handling
Flame Arresters
Storage and Handling of Hazardous Materials

Hazardous Materials and Conditions The chemical and physical situations that can result when operating with hazardous materials should be understood so these materials may be handled safely. This part covers the following:

Reactive Chemicals
Combustion and Flammability Hazards
Gas Explosions
Unconfined Vapor Cloud Explosions (UVCEs) and Boiling Liquid Evaporating Vapor Explosions (BLEVEs)
Dust Explosions
Static Electricity
Hazards of Vacuum
Hazards of Inert Gases
Gas Dispersion
Discharge Rates from Punctured Lines and Vessels

INHERENTLY SAFER DESIGN AND OTHER PRINCIPLES

INTRODUCTION: WHAT IS PROCESS SAFETY?

Process safety differs from the traditional approach to accident prevention in a number of ways (Lees, *Loss Prevention in the Process Industries,* 2d ed., Butterworth-Heinemann, 1996, p. 1.8):

- There is more concern with accidents that arise out of the technology.
- There is more emphasis on foreseeing hazards and taking action before accidents occur.

• There is more emphasis on a systematic rather than a trial-and-error approach, particularly on systematic methods of identifying hazards and of estimating the probability that they will occur, and their consequences.

• There is concern with accidents that cause damage to plants and loss of profit but do not injure anyone, as well as those that do cause injury.

• Traditional practices and standards are looked at more critically.

Process safety can be applied in any industry, but the term and the approach have been particularly widely used in the process industries, where it usually means the same as loss prevention.

Although process safety is as old as process engineering, it did not become recognized as a distinct branch of the subject until the 1960s, when a new generation of plants, larger than earlier ones and operating at higher temperatures and pressures, was involved in a number of serious fires and explosions. They made the industry realize that accident prevention needed the same sort of systematic and technical study as every other aspect of plant design and operation. Since then the number of publications and specialist journals, and the number and caliber of engineers specializing in the field, have grown rapidly.

INHERENTLY SAFER AND MORE USER-FRIENDLY DESIGN

For many years the usual procedure in plant design was to identify the hazards, by one of the systematic techniques described later or by waiting until an accident occurred, and then add on protective equipment to control future accidents or protect people from their consequences. This protective equipment is often complex and expensive and requires regular testing and maintenance. It often interferes with the smooth operation of the plant and is sometimes bypassed. Gradually the industry came to realize that, whenever possible, one should design user-friendly plants which can withstand human error and equipment failure without serious effects on safety (and output and efficiency). When we handle flammable, explosive, toxic, or corrosive materials we can tolerate only very low failure rates, of people and equipment—rates which it may be impossible or impracticable to achieve consistently for long periods of time.

The most effective way of designing user-friendly plants is to avoid, when possible, large inventories of hazardous materials in process or storage. "What you don't have, can't leak." This sounds obvious, but until the explosion at Flixborough, England, in 1974, little systematic thought was given to ways of reducing inventories. The industry simply designed a plant and accepted whatever inventory the design required, confident they could keep it under control. Flixborough weakened that confidence and the disaster ten years later at Bhopal, India, almost destroyed it. Plants in which we avoid a hazard, by reducing inventories or avoiding hazardous reactions, are usually called *inherently safer.*

The principle ways of designing inherently safer plants and other ways of making plants user-friendly are summarized as follows, with examples (Kletz, *Plant Design for Safety—A User-Friendly Approach,* Hemisphere, 1991).

Intensification This involves using so little hazardous material that it does not matter if it all leaks out. For example, at Bhopal, methyl isocyanate (MIC), the material that leaked and killed over 2000 people, was an intermediate for which it was convenient but not essential to store. Within a few years many companies had reduced their stocks of MIC and other hazardous intermediates.

As another example, at one time nitroglycerin (NG) was manufactured in batch reactors containing about a ton of raw materials and product. If the reactor got too hot, there was a devastating explosion. In modern plants, NG is made in a small continuous reactor containing about a kilogram. The severity of an explosion has been reduced a thousandfold, not by adding on protective devices, which might fail or be neglected, but by redesigning the process. The key change was better mixing, achieved not by a better stirrer, which might fail, but by passing one reactant (acid) through a device like a laboratory water pump so that it sucks in the other reactant (glycerin) through a sidearm. If the acid flow stops, the glycerin flow also stops, not through the intervention of a flow controller, which might fail, but as an inevitable result of the laws of physics (Bell, *Loss Prevention in the Process Industries,* Institution of Chemical Engineers Symposium Series No. 34, 1971, p. 50).

Intensification is the preferred route to inherently safer design, as the plants, being smaller, are also cheaper.

Substitution If intensification is not possible, then an alternative is to consider using a safer material in place of a hazardous one. Thus it may be possible to replace flammable solvents, refrigerants, and heat-transfer media by nonflammable or less flammable (high-boiling) ones, hazardous products by safer ones, and processes which use hazardous raw materials or intermediates by processes which do not. As an example of the latter, the product manufactured at Bhopal (carbaryl) was made from three raw materials. Methyl isocyanate is formed as an intermediate. It is possible to react the same raw materials in a different order so that a different and less hazardous intermediate is formed.

Attenuation Another alternative to intensification is attenuation, using a hazardous material under the least hazardous conditions. Thus large quantities of liquefied chlorine, ammonia, and petroleum gas can be stored as refrigerated liquids at atmospheric pressure instead of storing them under pressure at ambient temperature. (Leaks from the refrigeration equipment should also be considered, so there is probably no net gain in refrigerating quantities less than a few hundred tons.) Dyestuffs which form explosive dusts can be handled as slurries.

Limitation of Effects of Failures Limitation can be done by equipment design or change in reaction conditions, rather than by adding on protective equipment. For example:

• Spiral-wound gaskets are safer than fiber gaskets because, if the bolts work loose or are not tightened correctly, the leak rate is much lower.

• Tubular reactors are safer than pot reactors, as the inventory is usually lower and a leak can be stopped by closing a valve.

• Vapor phase reactors are safer than liquid phase ones, as the mass flow rate through a hole of a given size is much less. (This is also an example of attenuation.)

• A small, deep diked area around a storage tank is safer than a large, shallow one, as the evaporation rate is lower and the area of any fire is smaller.

• Heating media such as steam or hot oil should not be hotter than the temperature at which the materials being heated are liable to ignite spontaneously or react uncontrollably.

• Many runaway reactions can be prevented by changing the order of operations, reducing the temperature, or changing another parameter.

• Reduce the frequency of hazardous operations such as sampling or maintenance. What is the optimum balance between reliability and maintenance?

Simplification Simpler plants are friendlier than complex ones, as they provide fewer opportunities for error and less equipment which can fail. Some of the reasons for complication in plant design are:

• The need to control hazards. If one of the other actions already discussed, such as intensification, can be carried out, less add-on protective equipment is needed and plants will therefore be simpler.

• A desire for flexibility. Multistream plants with numerous crossovers and valves, so that any item can be used on any stream, have numerous leakage points, and errors in valve settings are easy to make.

• Lavish provision of installed spares with the accompanying isolation and changeover valves.

• Continuing to follow rules or practices which are no longer necessary.

• Design procedures which result in a failure to identify hazards until late in design. By this time it is impossible to avoid the hazard and all that can be done is to add on complex equipment to control it.

Knock-on Effects Plants should be designed so that those incidents that do occur do not produce knock-on or domino effects. This can be done, for example, by:

• Providing firebreaks, about 15 m wide, between sections, like firebreaks in a forest, to restrict the spread of fire.

• Siting equipment which is liable to leak outdoors so that leaks of flammable gases and vapors are dispersed by natural ventilation.

Indoors, a few tens of kilograms are sufficient for an explosion that can destroy the building. Outdoors, a few tons are necessary for serious damage. A roof over equipment such as compressors is acceptable, but walls should be avoided. (If leaks of toxic gases are liable to occur, it may be safer to locate the plant indoors, unless leaks will disperse before they reach the public or employees on other units.)

• Constructing storage tanks so that the roof-wall weld will fail before the base-wall weld, thus preventing spillage of the contents. In general, equipment designers should consider the way in which it is most likely to fail and, when possible, locate or design the equipment so as to minimize the consequences.

Avoiding Incorrect Assembly Plants should be designed so that incorrect assembly is difficult or impossible. For example, compressor valves should be designed so that inlet and exit valves cannot be interchanged.

Status Clear It should be possible to see at a glance if equipment has been assembled or installed incorrectly or whether a valve is in the open or shut position. For example:

• Check valves should be marked so that installation the wrong way round is obvious. It should not be necessary to look for a faint arrow hardly visible beneath the dirt.

• Gate valves with rising spindles are friendlier than valves with nonrising spindles, as it is easy to see whether they are open or shut. Ball valves are friendly if the handles cannot be replaced in the wrong position.

• Figure-eight plates (spectacle plates) are friendlier than slip plates (spades), as their positions are apparent at a glance. If slip plates are used, their projecting tags should be readily visible, even when the line is insulated. In addition, spectacle plates are easier to fit than slip plates, if the piping is rigid, and they are always available on the job. It is not necessary to search for them, as with slip plates.

Tolerance Whenever possible, equipment should tolerate poor installation or operation without failure. Expansion loops in pipework are more tolerant of poor installation than bellows are. Fixed pipes, or articulated arms, if flexibility is necessary, are friendlier than hoses. For most applications, metal is friendlier than glass or plastic.

Bolted joints are friendlier than quick-release couplings. The former are usually dismantled by a fitter after issue of a permit to work. One person prepares the equipment and another person opens it up; the issue of the permit provides an opportunity to check that the correct precautions have been taken. In addition, if the joints are unbolted correctly, any trapped pressure is immediately apparent and the joint can be remade or the pressure allowed to blow off. In contrast, many accidents have occurred because operators opened up equipment which was under pressure, without independent consideration of the hazards, using quick-release couplings. There are, however, designs of quick-release couplings which give the operator a second chance.

Low Leak Rate If friendly equipment does leak, it does so at a low rate, which is easy to stop or control. Examples already mentioned are spiral-wound gaskets, tubular reactors, and vapor phase reactors.

Ease of Control Processes with a flat response to change are obviously friendlier than those with a steep response. Processes in which a rise of temperature decreases the rate of reaction are friendlier than those with a positive temperature coefficient, but this is a difficult ideal to achieve in the chemical industry. However, there are a few examples of processes in which a rise in temperature reduces the rate of reaction. For example, in the manufacture of peroxides, water is removed by a dehydrating agent. If magnesium sulfate is used as the agent, a rise in temperature causes release of water by the agent, diluting the reactants and stopping the reaction (Gerrison and van't Land, *I&EC Process Design* **24,** 1985, p. 893).

Software In some programmable electronic systems (PES), errors are much easier to detect and correct than in others. Using the term *software,* in the wider sense, to cover all procedures, as distinct from hardware or equipment, some software is much friendlier than others. Training and instructions are obvious examples. As another example, if many types of gaskets or nuts and bolts are stocked, sooner or later the wrong type will be installed. It is better, and cheaper in the long run, to keep the number of types stocked to a minimum, even though more expensive types than are strictly necessary are used for some applications.

Designing Inherently Safer and More User-Friendly Plants The following actions are needed for the design of inherently safer and more user-friendly plants:

1. Designers need to be made aware that there is scope for improving the friendliness of the plants they design.
2. To achieve many of the changes previously suggested, it is necessary to carry out much more critical examination and systematic consideration of alternatives during the early stages of design than has been customary in most companies. Two studies are suggested: one at the conceptual or business analysis stage when the process is being chosen, and another at the flowsheet stage. For the latter, the usual hazard and operability (HAZOP) study questions may be suitable but with one difference. In a normal HAZOP on a line diagram, if, for example, "more of temperature" is being discussed, it is assumed that this is undesirable and ways of preventing it are sought. In a HAZOP of a flowsheet, it should be asked if "more of temperature" would be better. For the conceptual study, different questions are needed.
3. Many companies will say that they do consider alternatives during the early stages of plant design. However, what is lacking in many companies is a formal, systematic, structured procedure of the HAZOP type.

To achieve the more detailed improvements suggested here, it may be necessary to add a few questions to those asked during a normal HAZOP. For example, what types of valves, gaskets, and so forth, will be used?

INCIDENT INVESTIGATION AND HUMAN ERROR

Although most companies investigate accidents (and many investigate dangerous incidents in which no one was injured), these investigations are often superficial, and we fail to learn all the lessons for which we have paid the high price of an accident. The facts are usually recorded correctly, but often only superficial conclusions are drawn from them. Identifying the causes of an accident is like peeling an onion. The outer layers deal with the immediate technical causes and triggering events while the inner layers deal with ways of avoiding the hazard and with the underlying weaknesses in the management system (Kletz, *Learning from Accidents,* 2d ed., Butterworth-Heinemann, 1994).

Dealing with the immediate technical causes of a leak, for example, will prevent another leak for the same reason. If so little of the hazardous material can be used that leaks do not matter or a safer material can be used instead, as previously discussed, all significant leaks of this hazardous material can be prevented. If the management system can be improved, we may be able to prevent many more accidents of other sorts.

Other points to watch when drawing conclusions from the facts are:

1. Avoid the temptation to list causes we can do little or nothing about. For example, a source of ignition should not be listed as the primary cause of a fire or explosion, as leaks of flammable gases are liable to ignite even though we remove known sources of ignition. The cause is whatever led to the formation of a flammable mixture of gas or vapor and air. (Removal of known sources of ignition should, however, be included in the recommendations.) Similarly, human error should not be listed as a cause. See item 6 below.
2. Do not produce a long list of recommendations without any indication of the relative contributions they will make to the reduction of risk or without any comparison of costs and benefits. Resources are not unlimited and the more we spend on reducing one hazard, the less there is left to spend on reducing others.
3. Avoid the temptation to overreact after an accident and install an excessive amount of protective equipment or complex procedures which are unlikely to be followed after a few years have elapsed. Sometimes an accident occurs because the protective equipment available was not used; nevertheless, the report recommends installation of more protective equipment; or an accident occurs because complex procedures were not followed and the report recommends extra procedures. It would be better to find out why the original equipment was not used or the original procedures were not followed.
4. Remember that few, if any, accidents have simple causes.
5. When reading an accident report, look for the things that are not said. For example, a gland leak on a liquefied flammable gas pump caught fire and caused considerable damage. The report drew atten-

tion to the congested layout, the amount of redundant equipment in the area, the fact that a gearbox casing had been made of aluminum, which melted, and several other unsatisfactory features. It did not stress that there had been a number of gland leaks on this pump over the years, that reliable glands are available for liquefied gases at ambient temperatures, and, therefore, there was no need to have tolerated a leaky pump on this duty.

As another example, a fire was said to have been caused by lightning. The report admitted that the grounding was faulty but did not say when it was last checked, if it was scheduled for regular inspection, if there was a specification for the resistance to earth (ground), if employees understood the need for good grounding, and so on.

6. At one time most accidents were said to be due to human error, and in a sense they all are. If someone—designer, manager, operator, or maintenance worker—had done something differently, the accident would not have occurred. However, to see how managers and supervisors can prevent them, we have to look more closely at what is meant by human error:

a. Some errors are due to poor training or instructions: someone did not know what to do. It is a management responsibility to provide good training and instructions and avoid instructions that are designed to protect the writer rather than help the reader. However many instructions are written, problems will arise that are not covered, so people—particularly operators—should be trained in flexibility—that is, the ability to diagnose and handle unforeseen situations. If the instructions are hard to follow, can the job be simplified?

b. Some accidents occur because someone knows what to do but makes a deliberate decision not to do it. If possible the job should be simplified (if the correct method is difficult, an incorrect method will be used); the reasons for the instructions should be explained; checks should be carried out from time to time to see that instructions are being followed; and if they are not, this fact should not be ignored.

c. Some accidents occur because the job is beyond the physical or mental ability of the person asked to do it—sometimes it is beyond anyone's ability. The plant design or the method of working should be improved.

d. The fourth category is the commonest: a momentary slip or lapse of attention. They happen to everyone from time to time and cannot be prevented by telling people to be more careful or telling them to keep their minds on the job. All that can be done is to change the plant design or method of working to remove opportunities for error (or minimize the consequences or provide opportunities for recovery). Whenever possible, user-friendly plants (see above) should be designed which can withstand errors (and equipment failures) without serious effects on safety (and output and efficiency).

INSTITUTIONAL MEMORY

Most accidents do not occur because we do not know how to prevent them but because we do not use the information that is available. The recommendations made after an accident are forgotten when the people involved have left the plant; the procedures they introduced are allowed to lapse, the equipment they installed is no longer used, and the accident happens again. The following actions can prevent or reduce this loss of information.

- Include a note on "the reason why" in every instruction, code, and standard, and accounts of accidents which would not have occurred if the instruction, code, or standard had been followed.
- Describe old accidents, as well as recent ones, in safety bulletins and newsletters and discuss them at safety meetings.
- Follow up at regular intervals (for example, during audits) to see that the recommendations made after accidents are being followed, in design as well as operations.
- Make sure that recommendations for changes in design are acceptable to the design organization.
- On each unit keep a memory book, a folder of reports on past accidents, which is compulsory reading for new recruits and which others dip into from time to time. It should include relevant reports from other companies but should not include cuts and bruises.
- Never remove equipment before you know why it was installed. Never abandon a procedure before you know why it was adopted.
- Devise better information retrieval systems so that details of past accidents, in our own and other companies, and the recommendations made afterward are more easily accessible than at present.
- Include important accidents of the past in the training of young graduates and company employees. Suitable training material is available from the American Institute of Chemical Engineers and the U.K. Institution of Chemical Engineers (Crowl and Louvar, *Chemical Process Safety: Fundamentals and Applications,* Prentice Hall, 1990).

KEY PROCEDURES

Safety by design should always be the aim, but it is often impossible or too expensive and we then have to rely on procedures. Key features of all procedures are as follows:

- They should be as simple as possible and written in simple language, to help the reader, rather than protect the writer.
- They should be explained to and discussed with those who will have to carry them out, not just sent to them through the post.
- Regular checks and audits should be made to confirm that they are being carried out correctly. They will corrode more rapidly than the steelwork, once those in charge lose interest or turn a blind eye.

Many accidents have occurred because the two procedures discussed in the following sections were unsatisfactory or were not followed.

Preparation of Equipment for Maintenance The essential feature of this procedure is a permit-to-work system: the operating team prepares the equipment and writes down on the permit the work to be done, the preparation carried out, the remaining hazards, and the necessary precautions. The permit is then accepted by the person or group that will carry out the work and is returned when the work is complete. The permit system will not make maintenance 100 percent safe, but it does reduce the chance that hazards will be overlooked, list ways of controlling them, and inform those doing the job of the precautions they should take. The system should cover such matters as who is authorized to issue and accept permits to work, the training they should receive (not forgetting deputies), and the period of time for which permits are valid. It should also cover the following:

- *Isolation of the equipment under maintenance.* Poor or missing isolation has been the cause of many serious accidents. Do not rely on valves except for quick jobs; use blinds or disconnection and blanking unless the job is so quick that blinding (or disconnection) would take as long and be as hazardous as the main job. Valves used for isolation (including isolation while fitting blinds or disconnecting) should be locked shut (for example, by a padlock and chain). Blinds should be made to the same standard (pressure rating and material of construction) as the plant. Plants should be designed so that blinds can be inserted without difficulty; that is, there should be sufficient flexibility in the pipework or a slip ring or figure-eight plate should be used. Electricity should be isolated by locking off or removal of fuses. Do not leave them lying around for anyone to replace. Always try out electrical equipment after defusing to check that the correct fuses have been withdrawn.
- *Identification of the equipment.* Many accidents have occurred because maintenance workers opened up the wrong equipment. Equipment which is under repair should be numbered or labeled unambiguously. Temporary labels should be used if there are no permanent ones. Pointing out the correct equipment is not sufficient. "The pump you repaired last week is leaking again" is a recipe for an accident.
- *Freeing from hazardous materials.* Equipment which is to be repaired should be freed as far as possible from hazardous materials. Gases can be removed by sweeping out with nitrogen (if the gases are flammable) or air, water-soluble liquids by washing with water, and oils by steaming. Some materials, such as heavy oils and materials that polymerize, are very difficult or impossible to remove completely. Tests should be carried out to make sure that the concentration of any hazardous material remaining is below an agreed level. Machinery should be in the lowest energy state. Thus the forks of forklift trucks should be lowered and springs should not be compressed or extended. For some machinery, the lowest energy state is less obvious. Do not work under heavy suspended loads.

• *Jobs which raise special problems.* Such jobs might include entry to vessels and other confined spaces, hot work, and responsibilities of contractors.

• *Handover.* Permits should be handed over (and returned when the job is complete) person to person. They should not be left on the table for people to sign when they come in.

• *Change of intent.* If there is a change in the work to be done, the permit should be returned and a new one issued [Crowl and Grossel (eds.), *Handbook of Toxic Materials Handling and Management,* Chap. 12, Marcel Dekker, 1995].

Control of Plant and Process Modifications Many accidents have occurred because plant or process modifications had unforeseen and unsafe side effects (Sanders, *Management of Change in Chemical Plants: Learning from Case Histories,* Butterworth-Heinemann, 1993). No such modifications should therefore be made until they have been authorized by a professionally qualified person who has made a systematic attempt to identify and assess the consequences of the proposal, by hazard and operability study or a similar technique. When the modification is complete, the person who authorized it should inspect it to make sure that the design intention has been followed and that it "looks right." What does not look right is usually wrong and should at least be checked.

Unauthorized modifications are particularly liable to occur:

• During start-ups, as changes may be necessary to get the plant on line.

• During maintenance, as the maintenance workers may be tempted to improve the plant as well as repair it. They may suggest modifications but should put the plant back as it was unless a change has been authorized.

• When the modification is cheap and no financial authorization is necessary. Many seemingly trivial modifications have had tragic results.

• When the modification is temporary. Twenty-eight people were killed by the temporary modification at Flixborough, one of the most famous of all time (Lees, *Loss Prevention in the Process Industries,* 2d ed., Butterworth-Heinemann, 1996; p. 2).

• When one modification leads to another, and then another (Kletz, *Plant/Operations Progress* **5,** 1986, p. 136).

PROCESS SAFETY ANALYSIS

HAZARD ANALYSIS

General References: *ALOHA—Area locations of hazardous atmospheres* (computer program), Version 5.05 User's Manual, Hazardous Material Response Branch, National Oceanic and Atmospheric Administration (NOAA), Seattle, 1992. Applied Technology Corp. Chemical Manufacturers Association, *A Manager's Guide to Quantitative Risk Assessment,* December 1989. Arendt, JBF Associates, Inc., "Management of Quantitative Risk Assessment in the Chemical Industry," *Plant/Operations Progress,* vol. 9, no. 4, October 1990. Arthur D. Little, Inc., *FaultrEASE®,* 1991. *Chemical Exposure Index, Second Edition,* AIChE, New York, 1994. *CPQRA, Guidelines for Chemical Process Quantitative Risk Analysis,* CCPS-AIChE, New York, 1989. Crowl and Louvar, *Chemical Process Safety Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, N.J., 1990. Delboy, Dubnansky, and Lapp, "Sensitivity of Process Risk to Human Error in an Ammonia Plant," *Plant/Operations Progress,* vol. 10, no. 4, October 1991. *Development of an Improved LNG Plant Failure Rate Data Base,* prepared for Gas Research Inst., Chicago, September 1981. DNV Technica, PHAST and SAFETI, *Process Hazard Analysis Software Tools, Version 4.0,* Technica Inc., London, 1991. *Dow Fire and Explosion Index,* AIChE, New York, January 1994. Dowell, Rohm and Haas Texas, Inc., "Managing the PHA Team," *Process Safety Progress* **13,** no. 1, January 1994. *Fault Tree Handbook,* National Technical Information Service, January 1981. Golay and Todras, "Advanced Light-Water Reactors," *Scientific American,* April 1990. *Guidelines for Safe Storage and Handling of Highly Toxic Hazard Materials,* CCPS-AIChE, New York, 1989. HAZOP-PC, Risk and Hazard Analysis Software Version 3 (computer program), PrimaTech Inc., Columbus, Ohio, 1994. Knowlton, *Hazard and Operability Studies,* Chemetics International Co., Ltd., Vancouver, B.C., February 1989. Latino, *Strive for Excellence . . . the Reliability Approach,* Reliability Center Inc., 1980. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980. Moore, "The Design of Barricades for Hazardous Pressure Systems," *Nuc. Eng. Des.* **5,** 1550–1566, 1967. Munich Re (Münchener Rück) Report, "Losses in the Oil, Petrochemical and Chemical Industry: A Report," Munich, Germany, 1991. NFPA 69, *Explosion Prevention Systems,* National Fire Protection Association, Quincy, Mass., 1992. NFPA 704, *Standard System for the Identification of the Fire Hazards of Materials,* National Fire Protection Association, Quincy, Mass., 1990. Pape and Nussey, "A Basic Approach for the Analysis of Risks from Toxic Hazards," *The Institution of Chemical Engineering Symposium Series No. 93,* University of Manchester Institute for Science and Technology (England), 22–24 April 1985. PHAST, "Process Hazard Analysis Software Tool," DNV Technica Limited, London, October 1990. *Process Safety Progress,* AIChE, New York, January and April 1994 (issues devoted largely to chemical process safety management). *Reliability Guidelines for Process Equipment,* CCPS-AIChE, New York, 1989. Stern and Keller, "Human Error and Equipment Design in the Chemical Industry," *Professional Safety,* May 1991. Swain and Gutterman, *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications* (NUREG/CR-1278), Nuclear Regulatory Commission, Washington, 1983.

Introduction The meaning of *hazard* is often confused with *risk.* Hazard is defined as the inherent potential of a material or activity to harm people, property, or the environment. Hazard does not have a probability component.

There are differences in terminology on the meaning of *risk* in the published literature that can lead to confusion. *Risk* has been defined in various ways (*CPQRA,* 1989, pp. 3, 4). In this edition of the handbook, *risk* is defined as: "A measure of economic loss or injury in terms of both the incident likelihood and magnitude of loss or injury." *Risk* implies a probability of something occurring.

Definition of Terms Following are some definitions that are useful in understanding the components of hazards and risk (*CPQRA,* 1989, pp. 3, 4).

acceptable risk The average rate of risk considered tolerable for a given activity.

accident A specific combination of events or circumstances that leads to an undesirable consequence.

acute hazard The potential for injury or damage to occur as a result of an instantaneous or short-duration exposure to the effects of an accident.

chronic hazard The potential for injury or damage to occur as a result of prolonged exposure to an undesirable condition.

Cause-Consequence A procedure using diagrams to illustrate the causes and consequences of a particular scenario. They are not widely used because, even for simple systems, displaying all causes and outcomes leads to very complex diagrams.

Chemical Exposure Index (CEI) The CEI provides a method of rating the relative potential of acute health hazard to people from possible chemical release incidents.

consequence The direct, undesirable result of an accident, usually measured in health and safety effects, loss of property, or business costs, or a measure of the expected effects of an incident outcome case. For example, an ammonia cloud from a 10-lb/s leak under stability class D weather conditions and a 1.4-mi/h wind traveling in a northerly direction may injure 50 people.

consequence analysis Once hazards have been established, methods exist for analyzing their consequences (size of vapor cloud, blast damage radius, overpressure expected, etc.). This is independent of frequency or probability.

domino effect An incident which starts in one piece of equipment and affects other nearby items, such as vessels containing hazardous materials, by thermal blast or fragment impact. This can lead to escalation of consequences or frequency of occurrence. This is also known as a *knock-on effect.*

event An occurrence involving equipment performance or human action or an occurrence external to the system that causes system upset. An event is associated with an incident, either as a cause or a contributing cause of the incident, or as a response to an initiating event.

event sequence A specific, unplanned sequence of events composed of initiating events and intermediate events that may lead to an incident.

event tree Seeks to identify the ultimate consequence of an event, while fault tree analysis aims to identify the basic causes of a specific event. Event trees can grow quite large very quickly.

failure mode and effect analysis (FMEA) A hazard identification technique in which all known failure modes of components or features of a system are considered in turn and undesired outcomes are noted. It is usually used in combination with fault tree analysis. It is a complicated procedure, usually carried out by experienced risk analysts.

fault tree A method for representing the logical combinations of various system states which lead to a particular outcome, known as the *top event.*

Fire and Explosion Index (F&EI) The F&EI is used to rate the potential of hazard from fires and explosions.

frequency The rate at which observed or predicted events occur.

HAZOP HAZOP stands for "hazard and operability studies." This is a set of formal hazard identification and elimination procedures designed to identify hazards to people, process plants, and the environment. See subsequent sections for a more complete description.

incident The loss of containment of material or energy; for example, a leak of a flammable and toxic gas.

incident outcome The physical outcome of an incident; for example, a leak of a flammable and toxic gas could result in a jet fire, a vapor cloud explosion, a vapor cloud fire, a toxic cloud, etc.

probability The likelihood of the occurrence of events or a measure of the degree of belief, the values of which range from 0 to 1.

probability analysis Evaluates the likelihood of an event occurring. Using failure rate data for equipment, piping, instruments, and fault tree techniques, the frequency (events/year) can be quantified.

process hazard analysis (PHA) See subsequent section for description.

quantitative risk assessment (QRA) The systematic development of numerical estimates of the expected frequency and/or consequence of potential accidents associated with a facility or operation. Using consequence and probability analyses and other factors such as population density and expected weather conditions, QRA predicts the fatality rate for a given event. This methodology is useful for evaluation of alternates, but its value as an absolute measure of risk should be considered carefully.

risk analysis The development of a quantitative estimate of risk based on engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies.

risk assessment The process by which results of a risk analysis are used to make decisions, either through a relative ranking of risk reduction strategies or through comparison with risk targets. The terms *risk analysis* and *risk assessment* are often used interchangeably in the literature.

worst credible incident The most severe incident, considering only incident outcomes and their consequences, of all identified incidents and their outcomes.

Process Hazard Analysis (PHA) (Dowell, 1994, pp. 30–34.) The OSHA rule for Process Safety Management (PSM) of Highly Toxic Hazardous Chemicals, 29 CFR 1910.119, part (e), requires an initial PHA and an update every five years for processes that handle listed chemicals or contain over 10,000 lb (4356 kg) of flammable material. The PHA must be done by a team, must include employees such as operators and mechanics, and must have at least one person skilled in the methodology employed. Suggested methodologies from Process Safety Management are listed in Table 26-1.

The PHA must consider hazards listed in the PSM Rule, part (e), including information from previous incidents with potential for catastrophic consequences, engineering and administrative controls and consequences of their failure, facility siting, and human factors. Consequences of failure of controls must be considered.

TABLE 26-1 Process Hazard Analysis Methods Listed in the OSHA Process Safety Management Rule

- What-if
- Checklist
- What-if/checklist
- Hazard and operability study (HAZOP)
- Failure mode and effect analysis (FMEA)
- Fault tree analysis (FTA)
- An appropriate equivalent methodology

SOURCE: Dowell, 1994, pp. 30–34.

Documentation is important. Everything considered should be documented. "If it is not documented, then you didn't do it." (Dowell, 1994, pp. 30–34.) The key to PHA documentation is to do it right away before it gets cold. Periodic follow-up is needed by management and safety professionals to confirm that all recommendations have been addressed.

Hazard and Risk Assessment Tools The hazard and risk assessment tools used vary with the stage of the project from the early design stage to plant operations. Many techniques are available, both qualitative and quantitative, some of which are listed in the following section. Reviews done early in projects often result in easier, more effective changes.

Qualitative Tools for Hazard Analysis

SHEL (Safety, Health, Environmental, and Loss Prevention Reviews) These reviews are performed during design. The purpose of the reviews is to have an outsider's evaluation of the process and layout from safety, industrial hygiene, environmental, and loss prevention points of view. It is often desirable to combine these reviews to improve the efficiency of the use of time for the reviewers.

Checklists Checklists are simple means of applying experience to designs or situations to ensure that the features appearing in the list are not overlooked. Checklists tend to be general and may not be appropriate to a specific situation. They may not handle adequately the novel design or unusual process.

What-if At each process step, what-if questions are formulated and answered to evaluate the effects of component failures or procedural errors. This technique relies on the experience level of the questioner.

Failure Mode and Effect Analysis (FMEA) This is a systematic study of the causes of failures and their effects. All causes or modes of failure are considered for each element of a system, and then all possible outcomes or effects are recorded. This method is usually used in combination with fault tree analysis, a quantitative technique. FMEA is a complicated procedure, usually carried out by experienced risk analysts.

Cause-Consequence Diagram These diagrams illustrate the causes and consequences of a particular scenario. They are not widely used because, even for simple systems, displaying all causes and outcomes leads to very complex diagrams. Again, this technique is employed by experienced risk analysts.

Reactive Chemicals Reviews The process chemistry is reviewed for evidence of exotherms, shock sensitivity, and other instability, with emphasis on possible exothermic reactions. It is especially important to consider pressure effects—"Pressure blows up people, not temperature!" The purpose of this review is to prevent unexpected and uncontrolled chemical reactions. Reviewers should be knowledgeable people in the field of reactive chemicals and include people from loss prevention, manufacturing, and research.

Industrial Hygiene Reviews These reviews evaluate the potential of a process to cause harm to the health of people. It is the science of the anticipation, recognition, evaluation, and control of health hazards in the environment. It usually deals with chronic, not acute, releases and is involved with toxicity.

Toxicity is the ability to cause biological injury. Toxicity is a property of all materials, even salt, sugar, and water. It is related to dose and the degree of hazard associated with a material. The amount of a dose is both time and duration dependent. Dose is a function of exposure (concentration) and duration and is sometimes expressed as dose = $(\text{concentration})^n \times \text{duration}$, where n can vary from 1 to 4.

Industrial hygiene deals with hazards caused by chemicals, radiation, and noise. Routes of exposure are through the eyes, by inhalation, by ingestion, and through the skin. An industrial hygiene guide is based on exposures for an 8-hour day, 40-hour week and is to be used as a guide in the control of health hazards. It is not to be used as a fine line between safe and dangerous conditions. Types of controls used include:

- Engineering, such as containment, ventilation, and automation
- Administrative, such as use of remote areas and job rotation
- Protective equipment

Facilities Reviews There are many kinds of facilities reviews that are useful in detecting and preventing process safety problems. They include pre-start-up reviews (before the plant operates), new-plant reviews (the plant has started, but is still new), reviews of existing plants (safety, technology, and operations audits and reviews), management reviews, critical instrument reviews, and hazardous materials transportation reviews.

HAZOP (Knowlton, 1989; Lees, 1980; *CPQRA*, 1989, pp. 419–422). HAZOP stands for "hazard and operability studies." This is a set of formal hazard identification and elimination procedures designed to identify hazards to people, process plants, and the environment. The techniques aim to stimulate in a systematic way the imagination of designers and people who operate plants or equipment so they can identify potential hazards. In effect, HAZOP studies make the assumption that a hazard or operating problem can arise when there is a deviation from the design or operating intention. Corrective actions can then be made before a real accident occurs.

Some studies have shown that a HAZOP study will result in recommendations that are 40 percent safety-related and 60 percent operability-related. HAZOP is far more than a safety tool; a good HAZOP study also results in improved operability of the process or plant, which can mean greater profitability.

The primary goal in performing a HAZOP study is to identify, not analyze or quantify, the hazards in a process. The end product of a study is a list of concerns and recommendations for prevention of the problem, not an analysis of the occurrence, frequency, overall effects, and the definite solution. If HAZOP is started too late in a project, it can lose effectiveness because:

1. There may be a tendency not to challenge an already existing design.
2. Changes may come too late, possibly requiring redesign of the process.
3. There may be loss of operability and design decision data used to generate the design.

HAZOP is a formal procedure that offers a great potential to improve the safety, reliability, and operability of process plants by recognizing and eliminating potential problems at the design stage. It is not limited to the design stage, however. It can be applied anywhere that a design intention (how the part or process is expected to operate) can be defined, such as:

- Continuous or batch processes being designed or operated
- Operating procedures
- Maintenance procedures
- Mechanical equipment design
- Critical instrument systems
- Development of process control computer code

These studies make use of the combined experience and training of a group of knowledgeable people in a structured setting. Some key concepts are:

- *Intention*—defines how the part or process is expected to operate.
- *Guide words*—simple words used to qualify the intention in order to guide and stimulate creative thinking and so discover deviations. Table 26-2 describes commonly used guide words.
- *Deviations*—departures from the intention discovered by systematic application of guide words.
- *Causes*—reasons that deviations might occur.
- *Consequences*—results of deviations if they occur.
- *Actions*—prevention, mitigation, and control
  - —Prevent causes.
  - —Mitigate the consequence.
  - —Control actions, e.g., provide alarms to indicate things getting out of control; define control actions to get back into control.

The HAZOP study is not complete until response to actions has been documented. Initial HAZOP planning should establish the management follow-up procedure that will be used.

The guide words can be used on broadly based intentions (see Table 26-2), but when intentions are expressed in fine detail, some restrictions or modifications are necessary for chemical processes, such as:

No flow
Reverse flow
Less flow
More temperature
Less temperature
Composition change
Sampling
Corrosion/erosion

This gives a process plant a specific HAZOP guide-word list with a process variable, plant condition, or an issue.

HAZOP studies may be made on batch as well as continuous processes. For a continuous process, the working document is usually a set of flow sheets or piping and instrument diagrams (P&IDs). Batch processes have another dimension: time. Time is usually not significant with a continuous process that is operating smoothly except during start-up and shutdown, when time will be important and it will resemble a batch process. For batch processes, the working documents consist not only of the flow sheets or P&IDs but also the operating procedures. One method to incorporate this fourth dimension is to use guide words associated with time, such as those described in Table 26-3.

HAZOP studies involve a team, at least some of whom have had experience in the plant design to be studied. These team members apply their expertise to achieve the aims of HAZOP. There are four overall aims to which any HAZOP study should be addressed:

1. Identify as many deviations as possible from the way the design is expected to work, their causes, and problems associated with these deviations.
2. Decide whether action is required, and identify ways the problem can be solved.
3. Identify cases in which a decision cannot be made immediately and decide what information or action is required.
4. Ensure that required actions are followed through.

The team leader is a key to the success of a HAZOP study and should have adequate training for the job. Proper planning is important to success. The leader is actually a facilitator (a discussion leader and one who keeps the meetings on track) whose facilitating skills are just as important as technical knowledge. The leader outlines the boundaries of the study and ensures that the design intention is clearly understood. The leader applies guide words and encourages the team to discuss causes, consequences, and possible remedial actions for each deviation. Prolonged discussions of how a problem may be solved should be avoided.

Some people believe that it may be an advantage for the team leader not to have an intimate knowledge of the plant or process being studied in order to maintain neutrality. Ideally, the team leader should

TABLE 26-2 Some Guide Words Used in Conjunction with Process Parameters

Guide Word	Meanings	Comments
No, Not, None	Complete negation of design intentions	No part of intention is achieved and nothing else occurs
More of	Quantitative increases of any relevant physical parameters	Quantities and relevant physical properties such as flow rates, heat
Less of	Quantitative decreases	Same as above
As well as	Qualitative increase	All design and operating intentions are achieved as well as some additional activity
Part of	A qualitative decrease	Some intentions are achieved, some are not
Reverse	Logical opposite of intention	Activities such as reverse flow or chemical reaction, or poison instead of antidote
Other than	Complete substitution	No part of intention is achieved; something quite different happens

SOURCE: Knowlton, 1989.

TABLE 26-3 Guide Words Associated with Time

Guide word	Meaning
No time	Step(s) missed
More time	Step does not occur when it should
Less time	Step occurs before previous step is finished
Wrong time	Flow or other activity occurs when it should not

SOURCE: Knowlton, 1989.

be accompanied by a scribe or recorder, freeing the leader for full-time facilitating. The scribe should take notes in detail for full recording of as much of the meeting as is necessary to capture the intent of actions and recommendations.

Computer tools are available to aid information capture. In some cases, the facilitator may use the computer tool for recording, replacing the secretary. For example, PrimaTech offers a very useful computer program to aid in HAZOP studies (HAZOP-PC, 1994). Other excellent computer aids for HAZOP are also commercially available.

Team size is important. Less than three contributing members, excluding the secretary and leader, will probably reduce team effectiveness. A team size of five to eight, including the leader and scribe, is probably optimum.

The time required for HAZOP studies is significant. It has been estimated that each line or *node* (a node is usually a line or an item of equipment) may require in the range of about 30 minutes for an experienced team, although the time may vary widely. It should be recognized that the time required for HAZOP studies may not really be additional time for the project as a whole, particularly if started early enough in the design, and may actually save time on the project. It may make design of parts of the process more efficient, reduce the changes required later, and reduce the time required for safety and other reviews. It should make the safety reviews that should accompany any project much faster, as there will be fewer safety problems to discuss. It also should make possible smoother start-ups and make the process or plant safer and easier to operate, which will more than pay back the cost of the HAZOP study during the life of the plant. The results of a HAZOP study should be the basis for the operating discipline of a process, which in itself is a very valuable contribution.

Quantitative Tools for Hazard Analysis

Quantitative Fire and Explosion Index (F&EI) (*Dow Fire and Explosion Index Hazard Classification Guide,* 1994; Lees, 1980, pp. 149–160). The F&EI is used to rate the potential of hazard from fires and explosions. Its purpose is to quantify damage from an incident. It identifies equipment that could contribute to an incident and ways to mitigate possible incidents. It is a way to communicate to management the quantitative hazard potential.

The F&EI measures realistic maximum loss potential under adverse operating conditions. It is based on quantifiable data. It is designed for flammable, combustible, and reactive materials that are stored, handled, or processed. It does not address frequency (risk) except indirectly, nor does it address specific hazards to people except indirectly.

The goals of the F&EI are to raise awareness of loss potential and identify ways to reduce potential severity and potential dollar loss in a cost-effective manner. The index number has significance as a comparison and in calculations to estimate the *maximum probable property damage* (MPPD). It also provides a method for measuring the effect of outage (plant being shut down) on the business. It is easy for users to get credible results with a small amount of training.

Chemical Exposure Index (CEI) (*Chemical Exposure Index,* 1994). The CEI provides a method of rating the relative potential of acute health hazard to people from possible chemical release incidents. It may be used for conducting the initial process hazard analysis and it establishes the degree of further analysis needed. The CEI also may be used as part of the site review process.

The system provides a method of ranking one risk relative to another. It is not intended to define a particular containment system as safe or unsafe but provides a way of comparing toxic hazards. It deals with acute, not chronic, releases. The procedure focuses on the necessary degree of concern and will provide the opportunity for recommendations, improvements, and concurrence from the appropriate knowledgeable people. Flammability and explosion hazards are not included in this index.

The CEI and hazard distance determine the level of review that is necessary. To develop a CEI, the following information is needed:

- An accurate plot plan of the plant and surrounding area
- A simplified process flow sheet showing containment vessels, major piping, and quantity of chemicals
- Physical and chemical properties of the chemical, including boiling point, molecular weight, and flash point
- Pressure and temperature of materials contained
- Toxicity (acute health hazard rating)
- Quantity (volatilized portion)
- Distance (to area of concern)
- Process variables (temperature, pressure, reactivity)
- Sights, odors, or sounds that could cause public concern or inquiries, such as smoke and odors below hazardous levels—for example, mercaptans or amines
- ERPG/EEPG—usually ERPG-2 is used
- Definition of ERPG

The Emergency Response Planning Guidelines (ERPG) are values established by the American Industrial Hygiene Association and intended to provide estimates of chemical concentration ranges where one might reasonably anticipate observing adverse effects as follows:

ERPG-1 The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.

ERPG-2 The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing irreversible or other serious health effects or symptoms that could impair their ability to take protective action.

ERPG-3 The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

Factors to consider when calculating a CEI are:

1. Credible scenario for a release
2. The rate at which toxic materials would be released in a scenario

When these two factors are considered together, a possible release rate can be calculated.

When considering release scenarios, the most hazardous unit in a plant should be chosen, based on inventory and process conditions. The idea is to imagine the release of material in the fastest way that is reasonably possible. The worst realistic scenario should be considered. This can be based on the outcome of a review, from a HAZOP study or a hazard analysis. The time a scenario will take is almost always considered to be continuous, because after a few minutes a stable dispersion distance exists. Making the time longer will not necessarily change the hazard distance.

Quantitative Tools for Risk Analysis

Quantitative Risk Analysis (QRA) QRA is a technique that provides advanced quantitative means to supplement other hazard identification, analysis, assessment, control, and management methods to identify the potential for such incidents and to evaluate risk reduction and control strategies. QRA identifies those areas where operation, engineering, or management systems may be modified to reduce risk and may identify the most economical way to do it. The primary goal of QRA is that appropriate management actions, based on results from a QRA study, help to make facilities handling hazardous chemicals safer. QRA is one component of an organization's total process risk management. It allows the quantitative assessment of risk alternatives that can be balanced against other considerations.

Fault Tree Analysis Fault tree analysis permits the hazardous incident (called the *top event*) frequency to be estimated from a logic model of the failure mechanisms of a system. The top event is traced downward to more basic failures using logic gates to determine its causes and likelihood. The model is based on the combinations of fail-

ures of more basic system components, safety systems, and human reliability. The underlying technology is the use of relatively simple logic gates (usually AND and OR gates) to synthesize a failure model of a plant. AND gates combine input events, all of which must exist simultaneously for the output to occur. OR gates also combine input events, but any one is sufficient to cause the output. The top event frequency or probability is calculated from failure data of more simple events. The top event might be a boiling liquid evaporating vapor explosion (BLEVE), a relief system discharging to the atmosphere, or a runaway reaction.

NFPA Standard System for Identification of Health, Flammability, Reactivity, and Related Hazards (NFPA 704, Chaps. 2–5, 1990. This printed material is not the complete and official position of the National Fire Protection Association on the referenced subject, which is represented only by the standard in its entirety.)

This is a brief summary of NFPA 704 which addresses hazards that may be caused by short-term, acute exposure to a material during handling under conditions of fire, spill, or similar emergencies. This standard provides a simple, easily recognized, easily understood system of markings. The objective is to provide on-the-spot identification of hazardous materials.

These markings provide a general idea of the hazards of a material and the severity of these hazards as they relate to handling, fire protection, exposure, and control. This standard is not applicable to transportation or to use by the general public. It is also not applicable to chronic exposure. For a full description of this standard, refer to NFPA 704. The system identifies the hazards of a material in four principal categories: health, flammability, reactivity, and unusual hazards such as reactivity with water.

The degree of severity of health, flammability, and reactivity is indicated by a numerical rating that rates from zero (no hazard) to four (severe hazard). The information is presented in a square-on-point (diamond) field of numerical ratings. Information is presented as follows:

- Health rating in blue at nine o'clock
- Flammability rating in red at twelve o'clock
- Reactivity hazard rating in yellow at three o'clock
- Unusual hazards at six o'clock

Materials that demonstrate unusual reactivity with water are identified as W and materials that possess oxidizing properties shall be identified by the letters OX. Other special hazard symbols may be used to identify radioactive hazards, corrosive hazards, substances that are toxic to fish, and so on.

The use of this system will provide a standard method of identifying the relative degree of hazard that is contained in various tanks, vessels, and pipelines. Suggested applications include:

- All storage tanks outside the block limits of a plant.
- Within block limits of a plant, tanks or process vessels with a capacity of more than 5000 gal (19 m^3).
- Process lines 3 in (7.62 cm) and larger, containing material with a health or reactivity rating of two, three, or four, or a flammability rating of three or four. Lines containing materials with lower ratings can also be marked if desired.

The name of the material contained in the pipelines should be placed on all lines at the point where they enter or leave the block and at road crossings. Block limit valves and emergency block valves should be painted yellow.

For a detailed description of the degrees of severity of the ratings, see NFPA 704. Table 26-4 shows the system for identification of hazards. Figures 26-1, 26-2, and 26-3 show examples of arrangements for display of the NFPA 704 Hazard Identification System.

RISK ANALYSIS

General References: *Guidelines for Chemical Process Quantitative Risk Analysis,* CCPS-AIChE, New York, 1989. Arendt, "Management of Quantitative Risk Assessment in the Chemical Process Industry," *Plant Operations Progress,* vol. 9, no. 4, AIChE, New York, October 1990. CMA, "A Manager's Guide to Quantitative Risk Assessment," Chemical Manufacturers' Association, December 1989. EFCE, "Risk Analysis in the Process Industries," European Federation of Chemical Engineering, Publication Series no. 45, 1985. Lees,

TABLE 26-4 System for Identification of Hazards

	Identification of health hazard. Color code: Blue		Identification of flammability. Color code: Red		Identification of reactivity (stability). Color code: Yellow
Signal	Type of possible injury	Signal	Susceptibility of materials to burning	Signal	Susceptibility to release of energy
4	Materials that on short exposure could cause death or major residual injury	4	Materials that will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or that are readily dispersed in air and will burn readily	4	Materials that in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures
3	Materials that on short exposure could cause serious temporary or residual injury	3	Liquids or solids that can be ignited under almost all ambient temperature conditions	3	Materials that in themselves are readily capable of detonation or of explosive decomposition or reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water
2	Materials that on intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury	2	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur	2	Materials that readily undergo violent chemical change at elevated temperatures and pressures or which react violently with water or which may form explosive mixtures with water
1	Materials that on exposure would cause irritation but only minor residual injury	1	Materials that must be preheated before ignition can occur	1	Materials that are normally stable, but which can become unstable at elevated temperatures and pressures
0	Materials that on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material	0	Materials that will not burn	0	Materials that are normally stable, even under fire exposure conditions, and which are not reactive with water

SOURCE: Reprinted with permission from NFPA 704, *Standard System for the Identification of the Fire Hazards of Materials,* National Fire Protection Association, Quincy, Mass., 1990. This printed material is not the complete and official position of the National Fire Protection Association on the referenced subject, which is represented only by the standard in its entirety.

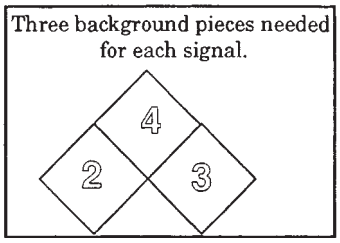


FIG. 26-1 For use where specified color background is used with numerals of contrasting colors. (*NFPA 704, 1990.*)

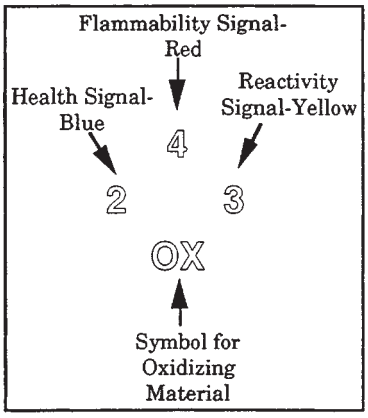


FIG. 26-2 For use where white background is used. (*NFPA 704, 1990.*)

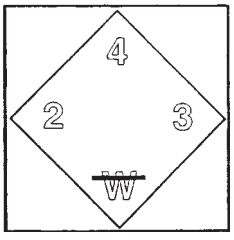


FIG. 26-3 For use where white background is used or for signs or placards. (*NFPA 704, 1990.*)

Loss Prevention in the Process Industries, Butterworths, Boston, 1980. World Bank, *Manual of Industrial Hazard Assessment Techniques,* Office of Environmental and Scientific Affairs, World Bank, Washington, D.C., 1985.

FREQUENCY ESTIMATION REFERENCES: *Guidelines for Process Equipment Reliability Data,* CCPS-AIChE, New York, 1989. Billington and Allan, *Reliability Evaluation of Engineering Systems: Concepts and Techniques,* Plenum Press, New York, 1983. Fussell, Powers, and Bennetts, "Fault Trees: A State of the Art Discussion," *IEEE Transactions on Reliability,* 1974. Roberts, N. H. et al., *Fault Tree Handbook,* NUREG-0492, Washington, D.C. Swain and Guttmann, *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications,* NUREG/CR-1278, USNRC, Washington, D.C., 1983.

CONSEQUENCE ESTIMATION REFERENCES: *Guidelines for Use of Vapor Cloud Dispersion Models,* CCPS-AIChE, New York, 1987. TNO, *Methods for the Calculation of the Physical Effects of the Escape of Dangerous Materials: Liquids and Gases* ("The Yellow Book"), Apeldoorn, The Netherlands, 1979.

RISK ESTIMATION REFERENCES: Health and Safety Executive, *Canvey—An Investigation of Potential Hazards from the Operations in the Canvey Island/Thurrock Area,* HMSO, London, 1978. Rasmussen, *Reactor Safety Study: An Assessment of Accident Risk in U.S. Commercial Nuclear Power Plants,* WASH-1400 NUREG 75/014, Washington, D.C., 1975. Rijnmond Public Authority, *A Risk Analysis of 6 Potentially Hazardous Industrial Objects in the Rijnmond Area—A Pilot Study,* D. Reidel, Boston, 1982.

Introduction The previous sections dealt with techniques for the identification of hazards and methods for calculating the effects of accidental releases of hazardous materials. This section addresses the methodologies available to analyze and estimate risk, which is a function of both the consequences of an incident and its frequency. The application of these methodologies in most instances is not trivial. A significant allocation of resources is necessary. Therefore, a selection process or risk prioritization process is advised before considering a risk analysis study.

Important definitions are as follows.

Markov model A mathematical model used in reliability analysis. For many safety applications, a discrete-state (e.g., working or failed), continuous-time model is used. The failed state may or may not be repairable.

Probit model A mathematical model of dosage and response in which the dependent variable (response) is a probit number that is related through a statistical function directly to a probability.

risk A measure of economic loss or human injury in terms of both incident likelihood (frequency) and the magnitude of the loss or injury (consequence).

risk analysis The development of an estimate of risk based on engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies. Incidents in the context of the discussion in this chapter are acute events which involve loss of containment of material or energy.

A typical hazard identification process, such as a hazard and operability (HAZOP) study, is sometimes used as a starting point for selection of potential major risks for risk analysis. Other selection or screening processes can also be applied. However major risks are chosen, a HAZOP study is a good starting point to develop information for the risk analysis study. A major risk may qualify for risk analysis if the magnitude of the incident is potentially quite large (high potential consequence) or if the frequency of a severe event is judged to be high (high potential frequency) or both. A flowchart which describes a possible process for risk analysis is shown in Fig. 26-4.

The components of a risk analysis involve the estimation of the frequency of an event, an estimation of the consequences (the extent of the material or energy release and its impact on population, property, or environment), and the selection and generation of the estimate of risk itself.

A risk analysis can have a variety of potential goals:

1. To screen or bracket a number of risks in order to prioritize them for possible future study
2. To estimate risk to employees
3. To estimate risk to the public
4. To estimate financial risk
5. To evaluate a range of risk reduction measures
6. To meet legal or regulatory requirements
7. To assist in emergency planning

The scope of a study required to satisfy these goals will be dependent upon the extent of the risk, the depth of the study required, and the level of resources available (mathematical models and tools and skilled people to perform the study and any internal or external constraints).

The objective of a risk analysis is to reduce the level of risk wherever practical. Much of the benefit of a risk analysis comes from the discipline which it imposes and the detailed understanding of the major contributors of the risk that follows. There is general agreement that if risks can be identified and analyzed, then measures for risk reduction can be effectively selected.

The expertise required in carrying out a risk analysis is substantial. Although various software programs are available to calculate the frequency of events or their consequences, or even risk estimates, engineering judgment and experience are still very much needed to produce meaningful results. And although professional courses are available in this subject area, there is a significant learning curve required not only for engineers to become practiced risk analysts, but

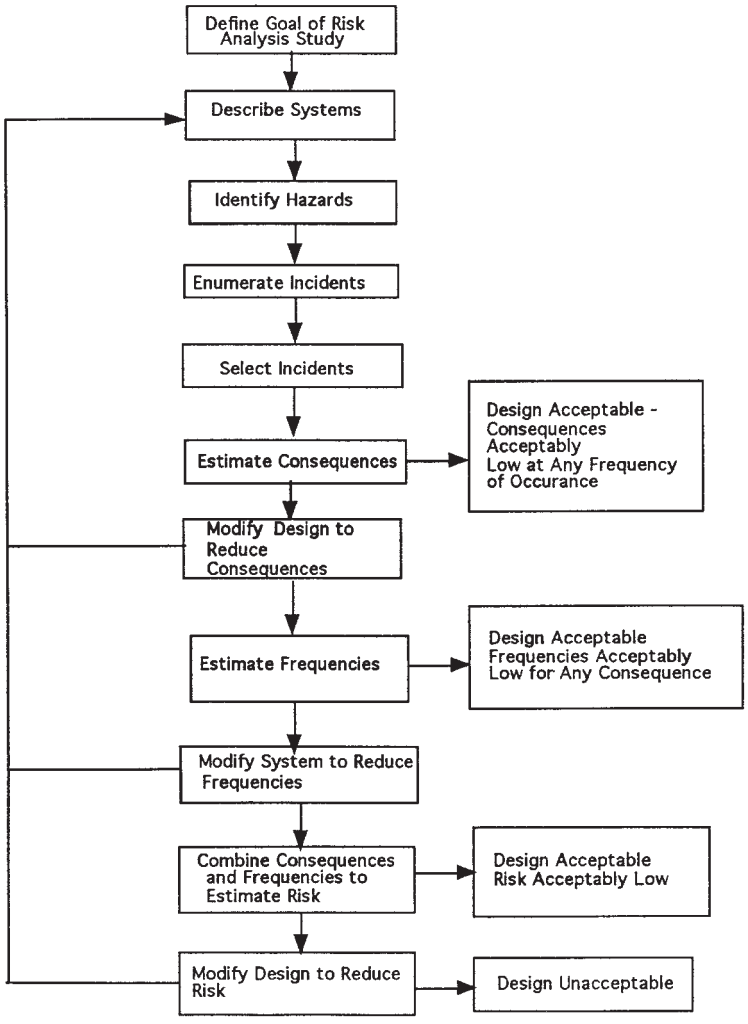


FIG. 26-4 One version of a risk analysis process. (*CCPS-AIChE, 1989, p. 13 by permission.*)

also for management to be able to understand and interpret the results. For these reasons, it may be useful to utilize a consultant organization in this field when a decision is made that a risk analysis is needed as a means to get started.

The analysis of a risk—that is, its estimation—leads to the assessment of that risk and the decision-making processes of selecting the appropriate level of risk reduction. In most studies this is an iterative process of risk analysis and risk assessment until the risk is reduced to some specified level. The subject of "acceptable" or "tolerable" levels of risk that could be applied to decision making on risks is a complex subject which will not be addressed in this section.

Frequency Estimation There are two primary sources for estimates of incident frequencies. These are historical records and the application of fault tree analysis and related techniques, and they are not necessarily applied independently. Specific historical data can sometimes be usefully applied as a check on frequency estimates of various subevents of a fault tree, for example.

The use of historical data provides the most straightforward approach to the generation of incident frequency estimates but is subject to the applicability and the adequacy of the records. Care should be exercised in extracting data from long periods of the historical record over which design or operating standards or measurement criteria may have changed.

An estimate of the total population from which the incident information has been obtained is important and may be difficult to obtain.

Fault tree analysis and other related event frequency estimation techniques, such as event tree analysis, play a crucial role in the risk analysis process. Fault trees are logic diagrams that depict how components and systems can fail. The undesired event becomes the top event and subsequent subevents, and eventually basic causes, are then developed and connected through logic gates. The fault tree is completed when all basic causes, including equipment failures and human errors, form the base of the tree. There are general rules for construction, which have been developed by practitioners, but no specific rules for events or gates to use. The construction of a fault tree is still more of an art than a science. Although a number of attempts have been made to automate the construction of fault trees from process flow diagrams or piping instrumentation diagrams, these attempts have been largely unsuccessful. (P. K. Andow, "Difficulties in Fault Tree Synthesis for Process Plant," *IEEE Transactions on Reliability* **R-29**(1): 2, 1980).

Once the fault tree is constructed, quantitative failure rate and probability data must be obtained for all basic causes. A number of equipment failure rate databases are available for general use. However, specific equipment failure rate data is generally lacking and,

therefore, data estimation and reduction techniques must be applied to generic databases to help compensate for this shortcoming. Accuracy and applicability of data will always be a concern, but useful results from quantifying fault trees can generally be obtained by experienced practitioners.

Human error probabilities can also be estimated using methodologies and techniques originally developed in the nuclear industry. A number of different models are available (Swain, "Comparative Evaluation of Methods for Human Reliability Analysis," GRS Project RS 688, 1988). This estimation process should be done with great care, as many factors can affect the reliability of the estimates. Methodologies using expert opinion to obtain failure rate and probability estimates have also been used where there is sparse or inappropriate data.

In some instances, plant-specific information relating to frequencies of subevents (e.g., a release from a relief device) can be compared against results derived from the quantitative fault tree analysis, starting with basic component failure rate data.

An example of a fault tree logic diagram using AND and OR gate logic is shown in Fig. 26-5.

The logical structure of a fault tree can be described in terms of boolean algebraic equations. Some specific prerequisites to the application of this methodology are as follows.

- Equipment states are binary (working or failed).
- Transition from one state to another is instantaneous.
- Component failures are statistically independent.
- The failure rate and repair rate are consistent for each equipment item.
- After repair, the component is returned to the working state.

Minimal cut set analysis is a mathematical technique for developing and providing probability estimates for the combinations of basic component failures and/or human error probabilities, which are necessary and sufficient to result in the occurrence of the top event.

A number of software programs are available to perform these calculations, given the basic failure data and fault tree logic diagram (AIChE-CCPS, 1989). Other less well known approaches to quantifying fault tree event frequencies are being practiced, which result in gate-by-gate calculations using discrete-state, continuous-time, Markov models (Doelp et al., "Quantitative Fault Tree Analysis, Gate-by-Gate Method," *Plant Operations Progress* **4**(3): 227–238, 1984).

Identification and quantitative estimation of common-cause failures are general problems in fault tree analysis. Boolean approaches are generally better suited to mathematically handle common-cause failures.

Event tree analysis is another useful frequency estimation technique used in risk analysis. It is a bottom-up logic diagram, which starts with an identifiable event. Branches are then generated, which lead to specific chronologically based outcomes with defined probabilities. Event tree analysis can provide a logic bridge from the top event, such as a flammable release into specific incident outcomes (e.g., no ignition, flash fire, or vapor cloud explosion). Probabilities for each limb in the event tree diagram are assigned and, when multiplied by the starting frequency, produce frequencies at each node point for all the various incident outcome states. The probabilities for all of the limbs at any given level of the event tree must sum to 1.0. Event trees are generally very helpful toward the generation of a final risk estimate.

Consequence Estimation Given that an incident (release of material or energy) has been defined, the consequences can be estimated. The general logic diagram in Fig. 26-6 illustrates these calculations for the release of a volatile hazardous substance.

For any specific incident there will be an infinite number of incident outcome cases that can be considered. There is also a wide degree of consequence models which can be applied. It is important, therefore, to understand the objective of the study to limit the number of incident outcome cases to those which satisfy that objective. An example of variables which can be considered is as follows.

- Quality, magnitude, and duration of the release
- Dispersion parameters
  wind speed
  wind direction
  weather stability
- Ignition probability (flammable releases)
  ignition sources/location
  ignition strength
- Energy levels contributing to explosive effects (flammable releases)
- Impact of release on people, property, or environment
  thermal radiation
  projectiles
  shock-wave overpressure
  toxic dosage
- Mitigation effects
  safe havens
  evacuation
  daytime/nighttime populations

Probit models have been found generally useful to describe the effects of incident outcome cases on people or property for more complex risk analyses. At the other end of the scale, the estimation of a distance within which the population would be exposed to a concentration of ERPG-2 or higher may be sufficient to describe the impact of a simple risk analysis.

Portions or all of the more complex calculation processes, using specific consequence models, have been incorporated into a few commercially available software packages (AIChE-CCPS, 1989). These programs should be used by risk analysts with extensive engineering experience, as significant judgment will still be required.

The output of these calculation processes is one or more pairs of an incident or incident outcome case frequency and its effect (consequence or impact).

Risk Estimation There are a number of risk measures which can be estimated. The specific risk measures chosen are generally related to the study objective and depth of study, and any preferences or requirements established by the decision makers. Generally, risk measures can be broken down into three categories: risk indices, individual risk measures, and societal risk measures.

Risk indices are usually single-number estimates, which may be used to compare one risk with another or used in an absolute sense compared to a specific target. For risks to employees the *fatal accident rate* (FAR) is a commonly applied measure. The FAR is a single-number index, which is the expected number of fatalities from a specific event based on 10^8 exposure hours. For workers in a chemical plant, the FAR could be calculated as follows:

$$\text{FAR} = \frac{10^8}{8760} \times f \times \frac{D}{N} \tag{26-1}$$

where FAR = fatal accident rate, expected number of fatalities from a specific event based on 10^8 exposure hours
f = frequency of the event in years^{-1}
D = expected number of fatalities, given the event
N = average number of exposed individuals on each shift

References are available which provide FAR estimates for various occupations, modes of transportation, and other activities (Kletz, "The Risk Equations—What Risk Should We Run?," *New Scientist*, May 12, pp. 320–325, 1977).

Figure 26-7 is an example of an individual risk contour plot, which shows the expected frequency of an event causing a specified level of harm at a specified location, regardless whether anyone is present at that location to suffer that level of harm.

The total individual risk at each point is equal to the sum of the individual risks at that point from all incident outcome cases.

$$\text{IR}_{x,y} = \sum_{i=1}^{n} \text{IR}_{x,y,i} \tag{26-2}$$

where $\text{IR}_{x,y}$ = total individual risk of fatality at geographical location x,y
$\text{IR}_{x,y,i}$ = individual risk of fatality at geographical location x,y from incident outcome case i
n = total number of incident outcome cases

A common form of societal risk measure is an F-N curve, which is normally presented as a cumulative distribution plot of frequency F

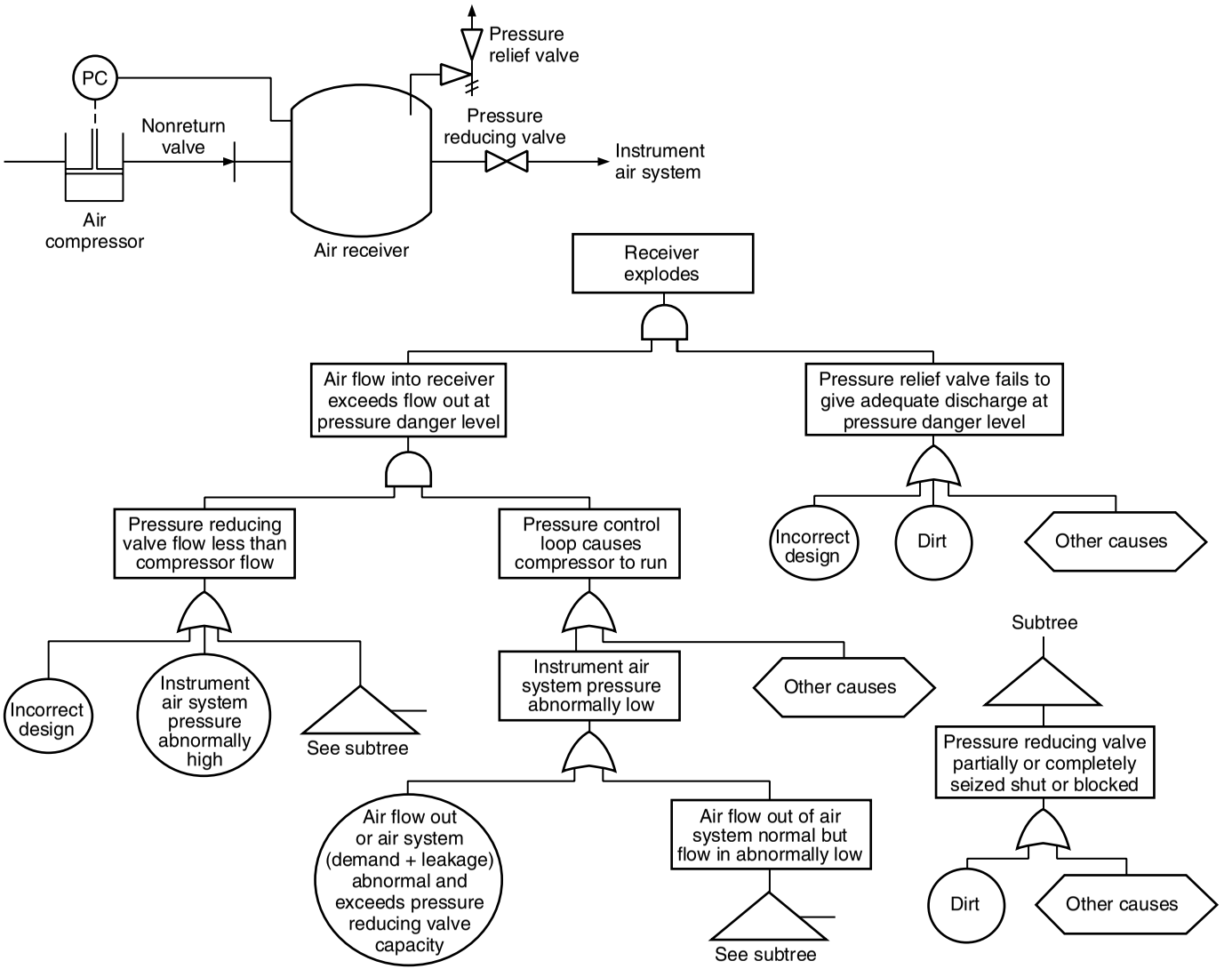


FIG. 26-5 Process drawing and fault tree for explosion of an air receiver. (*From Lees, 1980, pp. 200, 201, by permission.*)

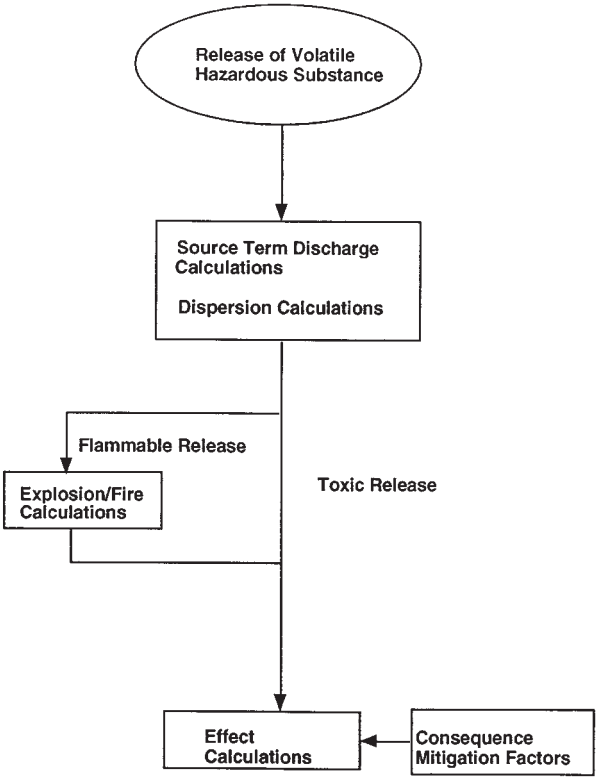


FIG. 26-6 Overall logic diagram for consequence analysis of volatile hazardous substances. (*CCPS-AIChE, 1989, p. 60.*)

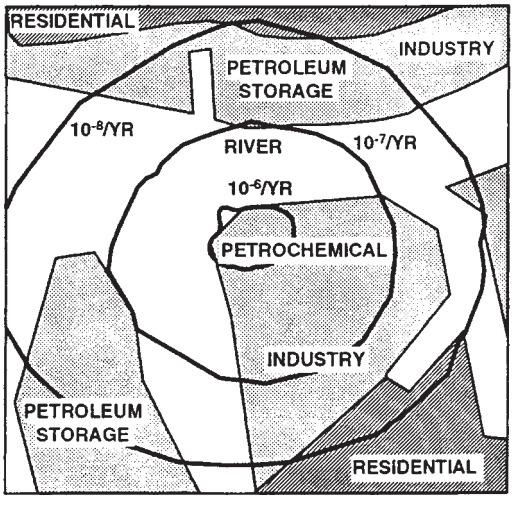


FIG. 26-7 Example of an individual risk contour plot. (*CCPS-AIChE, 1989, p. 269.*)

versus number of fatalities *N*. An example of this type of measure is shown in Fig. 26-8.

Any individual point on the curve is obtained by summing the frequencies of all events resulting in that number of fatalities or greater. The slope of the curve and the maximum number of fatalities are two key indicators of the degree of risk.

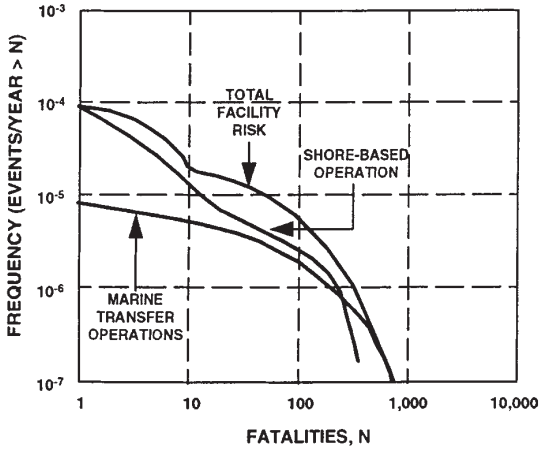


FIG. 26-8 Example of a societal risk F-N curve. (*AIChE-CCPS, 1989, p. 4.4.*)

For all risk measures it is possible to estimate the risk level of the current process as well as the risk levels from incorporation of various risk reduction alternatives. Management can then use this information as an important input in the final risk decision-making process.

GUIDELINES FOR ESTIMATING DAMAGE

Nomenclature

A	Projected area of fragment, breach area, or fragment cross-sectional area
a_a	Sound velocity in atmosphere
a_e	Sound velocity in high-pressure gas prior to vessel failure
B	Batch energy availability
d	Fragment diameter
E	Explosion energy available to generate blast and fragment kinetic energy, etc.
E_p	Critical perforation energy ($\frac{1}{2} MV_f^2$)
E_y	Young's modulus of elasticity
F	Dimensionless initial fragment acceleration
F	$P_e AR/Ma_e = P_e R/ma_e$ for vessel completely shattered into many small fragments
g	Acceleration due to gravity
h	Vessel wall thickness
k	Ratio of vessel outside diameter to internal diameter
L	Length of cylindrical vessel
M	Fragment mass
m	Mass per unit area of vessel shell
N	Length of cylindrical vessel forming rocketing tub fragment
N/m^2	Unit of pressure in SI system, N/m^2; also called pascal (Pa). One psi = 6.89476×10^3 Pa or 6.89476 kPa.
P	Liquid pressure
P_a	Atmospheric pressure
P_b	Dynamic vessel burst pressure
P_c	Pressure at expanding gas contact surface
P_e	Pressure at vessel failure
P_{inc}	Incident (side-on) blast pressure
P_r	Normally reflected (face-on) blast pressure
R	Vessel radius
r	Fragment radius = $(A/\pi)^{0.5}$
R_g	Range of fragment
t	Steel target thickness
U	$U_f + U_m$
u	Ultimate tensile strength of target steel
U_f	Fluid compression energy
U_m	Elastic strain energy in vessel walls
V	Volume of gas
V_f	Fragment velocity
V_L	Liquid volume
W	Equivalent mass of TNT
w	Unsupported span of steel target
X	Distance from wall of vessel to target

Nomenclature (*Concluded*)

	Greek letters
β_T	Fluid compressibility
γ	Ratio of specific heats of gas C_p/C_v
ϕ_0	Standard steady-state availability
ν	Poisson's ratio of vessel steel
	Subscripts
0	Reference state
1	Initial state
a	Environmental state
$1 \rightarrow a$	Denotes the path from state 1 to the environmental ambient state a

General References: Baker, Cox et al., "Explosion Hazards and Evaluation," *Fundamental Studies in Engineering 5,* Elsevier Science Publishing, New York, 1983. Kinney and Graham, *Explosive Shocks in Air,* 2d ed., Springer-Verlag, New York, 1985. Petes, *Annals, New York Academy of Sciences 1968,* vol. 152, pp. 283–316. Holden, *Assessment of Missile Hazards: Review of Incident Experience Relevant to Major Hazard Plant,* UKAEA SRD/HSE/R477, November 1988. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1996. Leslie and Birk, "State of the Art Review of Pressurized Liquefied Gas Container Failure Modes and Associated Projectile Hazards," *Journal of Hazard Materials* **28,** 1991, pp. 329–365. *ASCE Structural Analysis and Design of Nuclear Plant Facilities Manual and Reports on Engineering Practice* no. 58, 1980. Pritchard and Roberts, "Blast Effects from Vapour Cloud Explosions: A Decade of Progress," *Safety Science,* vol. 16 (3,4) 1993, pp. 527–548. "Explosions in the Process Industries," Major Haz. Monograph Series, *I. Chem. E.* (U.K.), 1994.

The availability of energy from an explosion can be approximately calculated in most cases but the method used depends upon the nature of the explosion.

Inert, Ideal Gas-Filled Vessels The energy available for external work following the rapid disintegration of the vessel is calculated by assuming that the gas within the vessel expands adiabatically to atmospheric pressure.

$$E = \frac{P_e V}{(g-1)}\left(\left[1-\left(\frac{P_a}{P_e}\right)^{(\gamma-1)/\gamma}\right]+(g-1)\left(\frac{P_a}{P_e}\right)\left[1-\left(\frac{P_a}{P_e}\right)^{-1/\gamma}\right]\right) \quad (26\text{-}3)$$

See Nomenclature table for definitions of terms.

In the case of thick-walled HP vessels, the strain energy in the vessel shell can contribute to the available energy, but for vessels below about 20 MN/m^2 (200 barg) it is negligible and can be ignored. If a Mollier chart for the gas is available, the adiabatic energy can be measured directly. This is the preferred method, but in many cases the relevant chart is not available.

The available energy is dissipated in several ways, e.g., the strain energy to failure, plastic strain energy in the fragments, kinetic energy of the fragments, blast wave generation, kinetic energy of vessel contents, heat energy in vessel contents, etc. For damage estimation purposes, the energy distribution can be simplified to:

$$E\ (\textstyle\int p\ dv)$$

30% blast 40% fragment kinetic energy 30% other dissipative mechanisms

Blast Characteristics Accurate calculation of the magnitude of the blast wave from an exploding pressure vessel is not possible, but it may be estimated from several approximate methods that are available.

One method of estimating the blast wave parameters is to use the TNT equivalent method, which assumes that the damage potential of the blast wave from a fragmenting pressure vessel can be approximated by the blast from an equivalent mass of trinitrotoluene (TNT). The method is not valid for the region within a few vessel diameters from the vessel. However, a rough approximation can be made outside this region by calculating an equivalent mass of TNT and utilizing its well-known blast properties. The term *equivalent mass* means the mass of TNT which would produce a similar damage pattern to that of the blast from the ruptured vessel. The energy of detonation of TNT is 4.5 MJ/kg (1.5×10^{-6} ft·lb/lb), so the TNT equivalent mass W is given by $W = 0.3E/4.5$ kg. Standard TNT data (Dept. of the Army, Navy, and Air Force, "Structures to resist the effects of accidental explosions," TM5-1300, NAVFAC P-397, AFM 88-22. U.S. Gov. Printing Office, vol. 2, November 1990, Figs. 2-7 and 2-15, or Kingery and Pannill, Memorandum Report No. 1518, Ballistic Research Laboratories, Aberdeen Proving Ground, U.S., April 1964) can then be used to determine the blast parameters of interest (Fig. 26-9). This method has limitations in the far field where the peak incident overpressure is less than 4 kN/m^2 (0.5 psi). In this region, local terrain and weather effects become significant.

The blast parameters also depend upon the physical location of the vessel. If the vessel is located close to or on the ground, then *surface-burst* data should be used. In other circumstances where the vessel is high in the air, either *free-air* or *air-burst* blast data may be used. These data are best presented in the form of *height-of-burst* curves (Petes, "Blast and Fragmentation Characteristics," *Ann. of New York Acad. of Sciences,* vol. 152, art. 1, fig. 3, 1968, p. 287). For incident blast pressures of 3×10^5 N/m^2 (3 bar) or less, using surface-burst data may overestimate the blast pressure by about 33 percent. Generally, pressure vessel ruptures rarely cause ground craters, so no allowance for cratering should be made.

Fragment Formation The way in which a vessel breaks up into several fragments as a consequence of an explosion or metal failure is impossible to predict. Consequently, in most cases it is necessary to assume several failure geometries and to assess the effect of each. The number of fragments formed is strongly dependent upon the nature of the explosion and the vessel design. For high-speed explosions—e.g., detonations or condensed phase explosions—the vessel frequently shatters into many fragments, but for slower-speed explosions—e.g., deflagrations and BLEVEs—generally fewer than ten fragments are formed, and frequently less than five. In the special case of pressurized liquefied gas vessels affected by fire, Holden and Reeves ("Fragment Hazards from Failures of Pressurized Liquefied Gas Vessels," *I. Chem. E. Sym. Series 93,* 1985, p. 213) suggest that with cylindrical vessels, up to four fragments could be projected and that greater fragmentation of spherical vessels occurred with the possibility that the number of fragments may increase with increasing vessel size.

Initial Fragment Velocity (V_f) The process of energy transfer from the expanding gas to the vessel fragments is not efficient and seldom exceeds 40 percent of the available energy. According to Baum ("The Velocity of Missiles Generated by the Disintegration of Gas Pressurized Vessels and Pipes," *Journal of Press. Vessel Technology,* Trans. ASME, vol. 106, November 1984, pp. 362–368), there is an

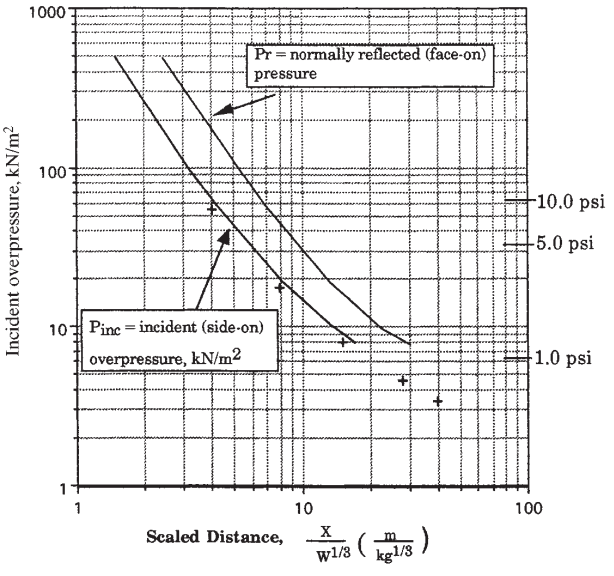


FIG. 26-9 Incident overpressure vs. scaled distance, surface burst. (*The "t" points are from Kingery and Pannill, Memo Report 1518 BRL. Adapted from Department of Army, Navy, and Air Force TM5-1300, NAVFAC P-397, AFM 88-22.*)

upper limit to the fragment velocity, which is taken to be the velocity of the contact surface between the expanding high-pressure gas and the surrounding atmospheric air. This is referred to as the *zero-mass* fragment velocity and, for most industrial low- to medium-pressure vessels, is less than about 1.3 Mach. It is calculated using ideal gas, one-dimensional shock tube theory and is given by the equation for the shock tube contact surface velocity (Wright, *Shock Tubes,* Methuen & Co., London, 1961).

$$\frac{V_f}{a_0} = -\frac{2}{(\gamma-1)}\left[\left(\frac{P_c}{P_e}\right)^{(\gamma-1)/2\gamma} - 1\right] \tag{26-4}$$

where P_c is determined from the relationship:

$$\frac{a_a(1-\mu_a)\left(\frac{P_c}{P_a}-1\right)}{a_e\left[(1+\mu_a)\left(\frac{P_c}{P_a}+\mu_a\right)\right]^{1/2}} = \frac{2}{(\gamma-1)}\left(1-\left(\frac{P_a}{P_e}\cdot\frac{P_c}{P_a}\right)^{(\gamma-1)/2\gamma}\right) \tag{26-5}$$

and

$$\mu_a = \frac{\gamma_a - 1}{\gamma_a + 1} \tag{26-6}$$

where P_c = pressure at expanding gas contact surface
a_a = sound velocity at ambient conditions
a_e = sound velocity in gas prior to vessel failure

The value of a_e may be approximated using physical property data for the specific gas at the temperature and pressure at the start of the expansion. Equation (26-5) must be solved using a trial-and-error method. Most fragments never achieve the zero-mass velocity and their velocity can be assessed using the correlations of Baum ("Disruptive Failure of Pressure Vessels: Preliminary Design Guidelines for Fragments Velocity and the Extent of the Hazard Zone," *J. Pressure Vessel Technology,* Trans. ASME, vol. 110, May 1988, pp. 168–176; Baum, "Rupture of a Gas-Pressurized Cylindrical Pressure Vessel. The Velocity of Rocketing Fragments," *J. Loss Prev. Process Ind.*, vol. 4, January 1991, pp. 73–86; Baum, "Velocity of a Single Small Missile Ejected from a Vessel Containing High Pressure Gas," *J. Loss Prev. Process Ind.*, vol. 6, no. 4, 1993, pp. 251–264).

The Baum correlations for several vessel failure modes are given in Eqs. (26-7) to (26-16).

End-Cap Released from a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 2F^{0.5} \tag{26-7}$$

where F is a dimensionless initial fragment acceleration given by

$$\frac{P_e AR}{Ma_e} \tag{26-8}$$

and A = projected area of fragment
M = fragment mass
R = vessel radius

Rocket Fragment from a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 2.18\left[F\left(\frac{L}{R}\right)^{0.5}\right]^{2/3} \tag{26-9}$$

where L = length of vessel and F is calculated using the area of the open end. For a more precise result, a correction factor to allow for the vessel opening time should be made (Baum, 1991).

Rocket Fragment from a Cylindrical Missile Pressurized with a Liquid at a Temperature Such That Rupture Initiates Flash Evaporation

$$\frac{V_f}{a_e} = 0.2\left(\frac{2E}{M}\right)^{0.5} \tag{26-10}$$

Range of experimental data:

$$\text{Water, } T_{sat} \sim 320°\text{C}, \ 145 \le \frac{P_e}{P_a} \le 155, \ N/L = 1.0, \ 12 \le L/R \le 24$$

The vessel is completely full of liquid and N is the length of the vessel forming the rocket fragment, with limited data.

Whole Vessel Driven by an Inert Ideal Gas Escaping through Axial Split

$$\frac{V_f}{a_e} = 0.17\left(\frac{2E}{M}\right)^{0.5} \tag{26-11}$$

Range of experimental data:

$$10 < \frac{P_e}{P_a} < 63, \ \gamma = 1.4, \ 4 < L/R < 6$$

Large, Single Fragment Ejected from Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 2F^{0.5} \tag{26-12}$$

Range of experimental data:

$$\frac{P_e}{P_a} = 100, \ \gamma = 1.4, \ L/R = 13.5, \ A^{0.5} > R$$

based upon two points only. End-cap equation (26-5) is probably adequate.

Single Small Fragment Ejected from a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = \left[2F\left(\frac{h}{R}\right)\right]^{0.5} + 0.96\left[F\left(\frac{r}{R}\right)\right]^{0.25} \tag{26-13}$$

where h = wall thickness
r = fragment radius, i.e., $r = (A/\pi)^{0.5}$

Range of experimental data:

$$20 < \frac{P_e}{P_a} < 300, \ \gamma = 1.4, \ r < 0.3\,R, \ h < 0.1\,R$$

Fragments Generated by Disintegration of a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 0.88\,F^{0.55} \tag{26-14}$$

Experimental data show no strong dependence on P_e/P_a or L/R.

Hemispherical Fragment Released from a Spherical Vessel Pressurized with a Liquid at a Temperature That on Rupture Initiates Flash Evaporation

$$\frac{V_f}{a_e} = 0.16\left(\frac{2E}{M}\right)^{1/2} \tag{26-15}$$

Range of experimental data:

$$\text{Water } T_{sat} \sim 230°\text{C}, \ 49.5 \le \frac{P_e}{P_a} \le 60.5$$

Limited data, vessel full of water.

Fragments Generated by Complete Shattering of Spherical Vessel Pressurized by an Inert Ideal Gas

$$\frac{V_f}{a_e} = 0.88\,F^{0.55} \tag{26-14}$$

Vessel Filled with Reactive Gas Mixtures Most cases of damage arise not from the vessel failing at its normal operating pressure but because of an unexpected exothermic reaction occurring within the vessel. This usually is a decomposition, polymerization, deflagration, runaway reaction, or oxidation reaction. In assessing the damage

potential of such incidents, the peak explosion or reaction pressure can often be calculated, and if this peak pressure P_e is then inserted into Eq. (26-3), the available energy can be assessed and the blast and fragment hazard determined. Where the expected peak explosion pressure P_e is greatly in excess of the vessel dynamic burst pressure, it is sufficient to increase the burst pressure to allow for the increase in vessel pressure during the period necessary for both the vessel to rupture and the fragments to be removed from the path of the expanding vessel contents. Where the gas pressure in the vessel is rising rapidly, the gas may reach a much higher pressure than the estimated dynamic burst pressure of the vessel. This effect is similar to the accumulation on a relief valve. It is, therefore, conservative to assume that the gas reaches the pressure calculated on the assumption of complete reaction. The reaction is assumed to go to completion before the containing vessel fails. However, there are reactions where it is simpler to calculate the energy availability using thermodynamic methods. The maximum energy released in an explosion can be assessed from the change in the Helmholz free energy ($-\Delta H = -\Delta E + T\Delta S$), but if the required data is not available, it may be necessary to use the Gibbs free energy ($\Delta F = \Delta H - T\Delta S$), which—especially in the case of reactions with little or no molal change, e.g., hydrocarbon/air oxidation—is similar to the Helmholz energy. It may sometimes be more convenient to calculate the batch energy availability [$B = \phi_0 + \Delta\phi_{1\to a} + \Delta(PV)_{1\to a} - P_a\Delta V_{1\to a}$] (Crowl, "Calculating the Energy of Explosion Using Thermodynamic Availability," *J. Loss Prev. Process Ind.*, **5,** no. 2, 1992, p. 109), which for an ideal gas becomes

$$B_1 = f_0 + f_{1\to a} + nRT_1\left[\left(\frac{P_a}{P_1}\right) - 1\right] \tag{26-16}$$

The energy partition between blast wave energy and fragment kinetic energy is as described in paragraph 1.

Vessels Completely Filled with an Inert High-Pressure Liquid A typical example is the pressure testing of vessels with water. The energy available to cause damage is the sum of the liquid compression energy and the strain energy in the vessel shell. The sudden release of this energy on vessel failure generally creates flying fragments but rarely any significant blast effects.

The fluid compression energy up to about 150 MN/m^2 (22,000 psig) can be estimated from $U_f = \frac{1}{2}\beta_T P^2 V_L$, where β_T is the liquid bulk compressibility, P is the liquid pressure, and V_L is the liquid volume. At higher pressure, this simple equation becomes too conservative and more complex methods of calculating the fluid compression energy are required. The elastic strain energy for cylindrical vessels, ignoring end closures, can be estimated from:

$$U_m = \frac{P^2 V_L}{2E(k^2 - 1)}\left[3(1 - 2\nu) + 2k^2(1 + \nu)\right] \tag{26-17}$$

where P = pressure of liquid
V_L = volume of liquid
E_y = Young's modulus of elasticity
ν = Poisson's ratio

Energy available $U = U_f + U_m$.

Only a small fraction of U is available to provide kinetic energy to the fragments. There are few data available, but in five incidents analyzed by High (unpublished data), no fraction was greater than 0.15. The fragment initial velocity can be assessed from $0.15\,U = \frac{1}{2}MV_f^2$.

Distance Traveled by Fragments There is no method available to estimate the distance traveled by an irregularly shaped, possibly tumbling, subsonic fragment projected at an unknown angle. A conservative approach is to assume that all the fragments are projected at an angle of 45° to the horizontal and to ignore the aerodynamic effects of drag and/or lift. The range R_g is then given by $R_g = V_f^2/g$, where g = gravitational acceleration.

This is too conservative to provide anything more than an upper bound. Some limited guidance is given by Scilly and Crowther ("Methodology for Predicting Domino Effects from Pressure Vessel Fragmentation," *Proc. Hazards Ident. and Risk Anal., Human Factors and Human Reliability in Process Safety,* Orlando, Fla., 15 Jan 1992, p. 5, sponsored by AIChE and HSE), where the range, for vessels with walls less than 20 mm (0.79 in), is 2.8 P_b with the range in meters and P_b as the vessel burst pressure in bars. Other sources are Baker (*Explosion Hazards and Evaluation,* Elsevier, 1983, p. 492) and Chemical Propulsion Information Agency (*Hazards of Chemical Rockets and Propellants Handbook,* vol. 1 NTIS, Virginia, May 1972, pp. 2-56, 2-60).

Fragment Striking Velocity It is generally impossible to assess the fragment velocity, trajectory, angle of incidence, and fragment attitude at the moment of striking a target; consequently, the conservative view is taken that the fragment strikes the target at right angles, in the attitude to give the greatest penetration, with a velocity equal to the initial velocity.

Damage Potential of Fragments In designing protection for fragment impact, there are two failure modes to be considered: local response and overall response. Local response includes penetration/perforation in the region of the impact. Overall response includes the bending and shear stresses in the total target element; i.e., will the whole target element fail regardless of whether the element is penetrated or perforated?

Local Failure The penetration or perforation of most industrial targets cannot be assessed using theoretical analysis methods, and recourse is made to using one of the many empirical equations. In using the equations, it is essential that the parameters of the empirical equation embrace the conditions of the actual fragment.

The penetrability of a fragment depends on its *kinetic energy density* (KED), given by

$$\text{KED} = \frac{1}{2}\frac{MV_f^2}{A} \tag{26-18}$$

where A is the fragment cross-sectional area. The KED is a useful comparative measure of a fragment's penetrability when comparing like with like. Several equations are given in the following sections.

Ballistics Research Laboratory (BRL) Equation for Steel Targets

$$E_p = 1.4 \times 10^9\,(dt)^{1.5} \tag{26-19}$$

where d is the fragment diameter, t is the steel target plate thickness, and E_p is the critical perforation energy in SI units (kg, m, m/s, J), when applied to fragments between 1 kg and 19.8 kg, impacting targets 1 mm to 25 mm (1 in) thick plate with velocities from 10 m/s to 100 m/s. Neilson (*Procedures for the Design of Impact Protection of Off-shore Risers and ESV's,* U.K. AEA [ed.], 1990) found a large scatter in the results, but most were within ±30 percent.

Stanford Research Institute (SRI) Equation for Steel Targets

$$E = \frac{dut^2}{10.3}\left(42.7 + \frac{w}{t}\right) \tag{26-20}$$

where, with the same notation as Eq. (26-14), w is the unsupported span of the target plate (m) and u the ultimate tensile strength of the target steel (N/m^2). The parameters for this equation are given by Brown ("Energy Release Protection for Pressurized Systems," part II, "Review of Studies into Impact/Terminal Ballistics," *Applied Mechanics Review,* vol. 39, no. 2, 1986, pp. 177–201) as $0.05 \le d \le 0.25m$, $414 \le u \le 482$ MN/m^2 for a fragment mass between 4.5 and 50 kg.

Overall Response The transition from local to overall response is difficult to define. High-velocity impact implies that the boundary conditions of the target have little influence on the local response (excluding reflected shock waves). If the fragment is small relative to the target, local response will dominate, but fragments that are of the same order of size as the target will produce an overall response. It is often necessary to consider both overall and local response. Low values of KED are associated with overall response. Design methods for dynamically applied loads are given by Newark ("An Engineering Approach to Blast Resistant Design," ASCE New York, 1953), Baker (see General References), or ASCE (*Manual and Reports on Engineering Practice,* no. 58, 1980).

Response to Blast Waves The effect of blast waves upon equipment and people is difficult to assess because there is no single blast wave parameter which can fully describe the damage potential of the

blast. Some targets respond more strongly to the peak incident overpressure and others to the impulse ($\int p\,dt$) of the blast. The blast parameters are usually based on the conservative assumption that the blast strikes the target normal to its surface, so that normal reflection parameters are used.

The pressure exerted by the blast wave on the target depends upon the orientation of the target. If the target surface faces the blast, then the target will experience the reflected or face-on blast pressure P_r, but if the target surface is side-on to the blast, then the target will experience the incident or side-on blast pressure P_{inc}. The reflected blast pressure is never less than double the incident pressure and can, for ideal gases, be as high as eight times the incident pressure. For most industrial targets where the incident pressure is less than about 17 kN/m^2 (25 psi), the reflected pressure is not more than 2.5 times the incident pressure.

Response of Equipment The response of equipment to blast is usually a combination of two effects: one is the displacement of the equipment as a single entity and the other is the failure of the equipment itself. The displacement of the equipment is an important consideration for small, unsecured items—e.g., empty drums, gas cylinders, empty containers. Most damage results from the failure in part or totally of the equipment or containing structure itself.

The blast parameters are usually based on the conservative assumption that the blast strikes the target normal to its surface, so that normal reflection parameters may be used.

The response of a target is a function of the ratio of the blast wave duration and the natural period of vibration of the target (T/T_n). Neither of these parameters can be closely defined.

Calculating the specific response of a specific target can generally be done only approximately. Accuracy is not justified when the blast properties are not well defined. A guide to the damage potential of condensed phase explosive blast is given in Table 26-5 (Scilly and High, "The Blast Effect of Explosions," *Loss Prevention and Safety Promotion in the Process Industries*, European Fed. of Chem. Eng., 337 Event, France, September 1986, table 2). Nuclear data is available (Table 26-6) (Walker, "Estimating Production and Repair Effort in Blast-damaged Petroleum Refineries," *Stanford Research Inst.,* July 1969, fig. 5, p. 45), which is based upon long positive-duration blast (±6 s). This suggests that the Walker data will be conservative for the much shorter duration blast from accidental industrial explosions.

A blast incident overpressure of 35 kN/m^2 (5 psi) is often used to define the region beyond which the damage caused will be minor and not lead to significant involvement of plant and equipment beyond the 35 kN/m^2 boundary.

Response of People The greatest hazard to people from blast is generally from the deceleration mechanism after people have been blown off their feet and they become missiles. This occurs at an incident overpressure of about 27 kN/m^2 (4.0 psi) for long positive-duration nuclear weapon blasts. People have more blast resistance than most equipment and can survive incident overpressures of 180 kN/m^2 (27 psi) (Bowen, Fletcher, and Richmond, DASA-2113, Washington, D.C., October 1968), even for long-duration blasts.

TABLE 26-5 Damage Effects

Incident, psi	Pressure, kPa	Damage effects
10	70	Damage to most refineries would be severe, although some pumps, compressors, and heat exchangers could be salvaged. All conventional brick buildings would be totally destroyed. Rail wagons (rail cars) overturned. Storage tanks ruptured. Fatalities certain.
5.0	34	Brick buildings severely damaged, 75% external wall collapse. Fired heaters badly damaged. Storage tanks leak from base. Threshold for eardrum damage to people. Domino or knock-on radius. Pipe bridges may move.
2.0	14	Doors and windows removed. Some frame distortion to steel frame buildings and cladding removed. Some electrical/instrument cables broken.*
1.0	7	Lethal glass fragments. Limit for public housing, schools, etc.
0.3	2	About 50% domestic glass broken.

*1% probability electrical cables broken at 2.0 psi inc. 99% probability electrical cables broken at 3.6 psi inc.

PROJECT REVIEW AND AUDIT PROCESSES

General References: Center for Chemical Process Safety (CCPS), *Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples,* AIChE, September 1992. CCPS, *Guidelines for Technical Management of Chemical Process Safety,* AIChE, 1989. CCPS, *Guidelines for Auditing Process Safety Management Systems,* AIChE, 1993.

Introduction Review and audit processes are used in the chemical process industry to evaluate, examine, and verify the design of process equipment, operating procedures, and management systems. These processes assure compliance with company standards and guidelines as well as government regulations. Reviews and audits can encompass the areas of process and personnel safety, environmental and industrial hygiene protection, quality assurance, maintenance procedures, and so on.

To distinguish between a review and an audit, some definitions will be provided. A review is a critical examination or evaluation of any operation, procedure, condition, event, or equipment item. Reviews can take many forms and be identified as project reviews, design reviews, safety reviews, pre-start-up reviews, and so on. The following discussion of the review process will deal with project reviews associated with capital projects and focus on the area of process safety.

An audit is a formal, methodical examination and verification of an operation, procedure, condition, event, or series of transactions. The verification element of an audit makes it distinctive from a review. A project review will *recommend* design, procedural, maintenance, and management practices to minimize hazards and reduce risk while meeting company standards and government regulations. An audit will *verify* that the design, the procedures, and the management systems are actually in place, and are being maintained and used as intended. In fact, it is not uncommon for an audit to be done on a review process, which is a management system, to verify that the elements of the review process are being followed.

The following sections will describe the project review and audit processes separately, addressing the why, when, and how for each process.

Project Review Process The scope of capital projects can be large, involving the construction of new plants with new technologies and products, or small, involving minor changes to existing facilities. In either case, project safety reviews can be used to evaluate and examine the process design, operating procedures, and process control scheme for process hazards, conformance to company standards and guidelines, and compliance with government regulations. Some objectives of the review process (CCPS, 1992, p. 53) are: (1) identify equipment or process changes that could introduce hazards, (2) evaluate the design basis of control and safety systems, (3) evaluate operating procedures for necessary revisions, (4) evaluate the application of new technology and any subsequent hazards, (5) review the adequacy of maintenance and safety inspections, and (6) evaluate the consequences of process deviations and determine if they are acceptable (CCPS, 1989, p. 46).

The project review process should be integrated with the development of the project from the conceptual stage to the start-up stage (CCPS, 1989, p. 46). Figure 26-10 depicts the various stages of a capital project. The size and complexity of a project will determine if the project progresses through all these stages and, in the same manner, determine the number and type of reviews that are needed. The earlier in a project that a review can be used to identify required changes, the less costly the change will be to implement. For example, reviews held at the research stage of a project can be beneficial in choosing the least hazardous technology and contribute to an inherently safer process design that needs fewer add-on safety systems.

As the project progresses, more information is available; therefore, the review technique used can be different at each stage of the project. The use of various hazard evaluation techniques, such as checklist analyses, relative rankings, what-if analyses, and hazard and operabil-

TABLE 26-6 Blast Overpressure Effects on Vulnerable Refinery Parts

Equipment	Overpressure (psi)																							
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	12.0	14.0	16.0	18.0	20.0	>20.0
Control house: steel roof	*a*	*c*	*d*				*h* →																			
Control house: concrete roof	*a*	*e p*	*d*				*n*													*e* →						
Cooling tower	*b*		*f*				*o* →																			
Tank: cone roof		*d*				*k* →							*u* →													
Instrument cubicle			*a*			*i m*						*t* →														
Fired heater				*g*	*i*					*t* →																
Reactor: chemical				*a*				*i*					*p*					*t* →								
Filter				*h*					*i*										*v*		*t* →					
Regenerator						*i*				*i p*					*t* →											
Tank: floating roof						*k*							*u*												*d* →	
Reactor: cracking							*i*							*i*							*t* →					
Pipe supports							*p*					*s o* →														
Utilities: gas meter									*q* →																	
Utilities: electric transformer									*h*						*l*					*t* →						
Electric motor										*h*								*l*								*v* →
Blower										*q*										*t* →						
Fractionation column											*r*			*t* →												
Pressure vessel: horizontal												*p i*						*t* →								
Utilities: gas regulator												*i*								*m q* →						
Extraction column													*i*							*v*	*t* →					
Steam turbine															*l*						*m*	*s*				*v* →
Heat exchanger															*i*			*t* →								
Tank: sphere																*i*						*i*	*t* →			
Pressure vessel: vertical																					*i*	*t* →				
Pump																					*i*		*v* →			

CODE:

a	Windows and gauges break.	*h*	Debris-missile damage occurs.	*p*	Frame deforms.
b	Louvers fall at 0.3–0.5 psi.	*i*	Unit moves and pipes break.	*q*	Case is damaged.
c	Switchgear is damaged from roof collapse.	*j*	Bracing fails.	*r*	Frame cracks.
		k	Unit uplifts (half-filled).	*s*	Piping breaks.
d	Roof collapses.	*l*	Power lines are severed.	*t*	Unit overturns or is destroyed.
e	Instruments are damaged.	*m*	Controls are damaged.	*u*	Unit uplifts (0.9 filled).
f	Inner parts are damaged.	*n*	Block walls fail.	*v*	Unit moves on foundation.
g	Brick cracks.	*o*	Frame collapses.		

SOURCE: F. E. Walker, "Estimating Production and Repair Effort in Blast Damaged Petroleum Refineries," *SRI,* July 1969.

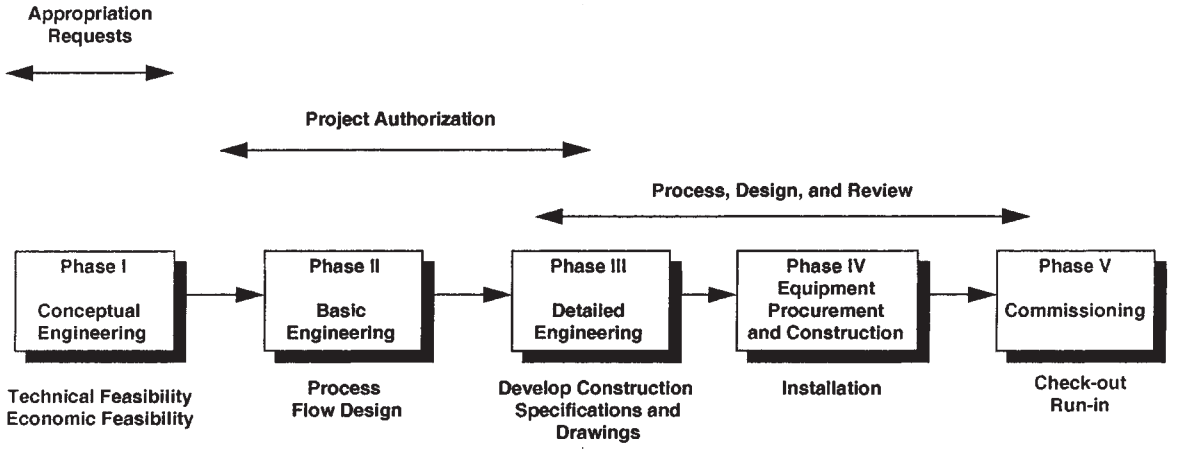


FIG. 26-10 The phases of a capital project. (*CCPS, 1989 by permission of AIChE.*)

ity studies, is documented in *Guidelines for Hazard Evaluation Procedures: Second Edition with Worked Examples* (CCPS, 1992). The need to use more quantitative techniques for hazard evaluation may be identified during these reviews, and become an action item for the project team.

The project review process involves multiple steps that should be defined in management guidelines (CCPS, 1993, pp. 57–61). The steps include: (1) review policy, (2) review scheduling, (3) review technique, (4) review team representation, (5) review documentation, (6) review follow-up, (7) review follow-up verification, and (8) review procedures change management. These steps define how a review, whether it be a safety review, environmental review, pre-start-up review, or whatever, is conducted and how closure of review action items is achieved.

Review Policy The review policy should establish when project safety reviews should be done. All capital projects, large or small, should have one or more safety reviews during the course of the project. The number and types of review should be stated in a management policy. Any reasons for exceptions to the policy should be documented as well. The policy should address not only projects internal to a company, but also any joint ventures or turnkey projects by outside firms.

Review Scheduling A review scheduling procedure should be established that documents who is responsible for initiating the review and when the review(s) should occur during the project. The scheduling needs to balance availability of process information, review technique used, and the impact of potential review action items on project costs (i.e., early enough to minimize the cost of any potential changes to the process). The actual amount of time needed for the review should also be stated in the procedure. On the basis of the number of project reviews required and the estimated time needed for each review, the project cost estimate should include the cost for project reviews as part of the total cost for the project.

Review Team The project review should be conducted by a functionally diverse team. The team should consist of a team leader to organize and lead the team review, a scribe or secretary to record and issue a review summary with action items, and functional experts in fields relevant to the project such as safety, environmental, and industrial hygiene (CCPS, 1993, p. 58). The team leader should be experienced in the use of the selected review technique with leadership skills and no direct involvement with the project under review. The review procedure should address the minimum requirements for team leaders and team members. Some typical requirements could be years of experience, educational background, and training in the review technique. Responsibilities should be clearly defined for initiating the review, assigning the review team, recording the team findings, and monitoring follow-up of team recommendations.

Review Techniques The review techniques used at the various stages of a project should be selected based on the amount of process information and detail available. Figure 26-11 depicts some typical review techniques at the various stages of a capital project. A detailed description, including the type and amount of process information required, for each review technique can be found in *Guidelines for Hazard Evaluation Procedures: Second Edition with Worked Examples* (CCPS, 1992). The process information required for the review should be defined and documented in the review guidelines. Up-to-date and accurate process information is essential to conducting a successful review.

Review Documentation The project review team leader has the ultimate responsibility for documenting the results of the project review. This responsibility may be delegated to a team scribe or secretary to record the review minutes and issue a summary report with listed action items. The action items could address exceptions to company or industry standards and government regulations, review team recommendations based on experience and knowledge, and further issues for study that could not be resolved during the review session.

The summary report should have a standard format and could contain a short project scope summary, a listing of review team members by function, a listing of project team members present, a meeting agenda or checklist of topics reviewed by the team, and a list of concerns and action items for project team follow-up. The distribution list for the summary report should be established and include the review team, project team, and any personnel outside the project team who have follow-up responsibilities for any of the action items. Also, include on the distribution list any appropriate management personnel, whether they be project team supervisors, manufacturing managers, or engineering managers. The documentation for the review should be archived in a process plant file with the appropriate records retention time (e.g., the life of the plant).

Review Follow-up An important element (maybe the most important) of the review process is the follow-up to action items. The project review will result in a list of potential concerns and action items, but, without follow-up, the issues will never be resolved and implemented. A person(s) should be assigned to each action item, preferably at the time of the project review. The person(s) assigned should have a combination of knowledge, resources, and authority to do a proper job in following up on the action items (CCPS, 1993, p. 59). The total action item list should not be assigned to one person, since it may overwhelm one individual. Depending on the number of action items generated, prioritizing the action item list may be helpful and a responsibility the review team can assume.

Progress on the action items should be documented in periodic progress reports to the review team leader or others assigned that functional responsibility. If no one is assigned the responsibility of tracking this progress, completion of the action list will probably be relegated to a lower priority and not be done.

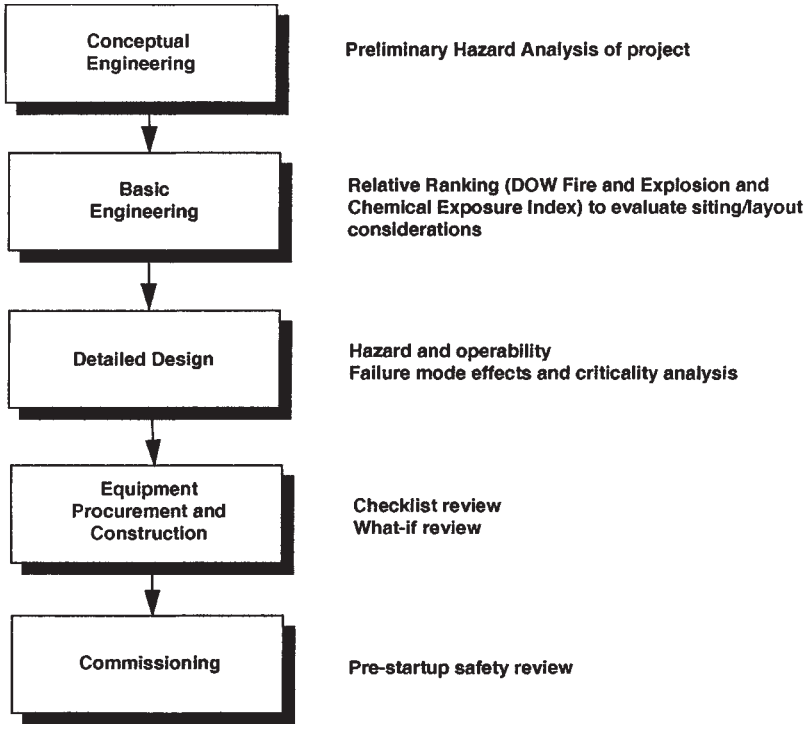


FIG. 26-11 Hazard evaluation at various project stages. (*CCPS, 1993, by permission of AIChE.*)

Changes made to the process as a result of the project review may require a similar review before implementation, especially if the change is significant.

Review Follow-up Verification In addition to someone tracking the follow-up through progress reports, responsibility should be assigned to verify that any process changes were actually made in the field. This verification can be done by a review team as part of a process pre-start-up review. It could also be part of the project team management responsibility or assigned to a particular functional (i.e., safety and loss prevention) representative. The closure of the review process is complete once implementation is verified.

On rare occasions, the resolution of project review concerns or action items is a point of contention between review team and project team members. In such a case, a management structure must be in place to arbitrate such disputes.

Review Procedure Change Management The project review process can require changes in policy and procedures at certain times. Therefore, the procedures should provide a management-of-change mechanism for suggesting changes and assign a person responsible for initiating and implementing any necessary changes.

Audit Process Audits in the chemical process industry can be focused on process safety, process safety management, environmental, and health areas. The discussion in this section will focus on the process safety and process safety management area, but it should be recognized that the process can be applied to the other areas as well. "Process safety audits are intended to provide management with increased assurance that operating facilities and process units have been designed, constructed, operated, and maintained such that the safety and health of employees, customers, communities, and the environment are being properly protected" (CCPS, 1989, p. 133). Process safety management system audits "provide increased assurance that operating units have appropriate systems in place to manage process risk" (CCPS, 1989, p. 130). The audit process described in the following can be used to verify the implementation of equipment designs, operating and maintenance procedures, control systems, and management systems to meet the previously stated intentions.

The key steps in the audit process are outlined according to preaudit activities, audit activities, and postaudit activities in Fig. 26-12. These activities are described in detail in *Guidelines for Auditing Process Safety Management Systems* (CCSP, 1993) and will be only briefly discussed in this section.

Preaudit Process Prior to the actual on-site audit, some preliminary activities should take place. These activities include selecting the facilities to be audited, scheduling the audit, selecting the audit team, and planning the audit. The selection criteria may be random, based on potential hazards of the facilities or the value of the facilities from a business standpoint. Audit scheduling must account for the availability of key facility personnel and audit team members, operational mode of the facility (i.e., it should be in normal operation), and the lead time required to obtain background information that may require advance visits to the facility and preaudit interviews. The audit team members should possess the technical training and experience to understand the facilities being audited. They should be knowledgeable in the auditing process and in the appropriate regulations and standards that will apply to the facilities. They should also be impartial and objective about audit findings. The audit plan should define the audit scope (what parts of the facility will be covered, what topics, who will do it, etc.), develop an audit protocol that is a step-by-step guide to how the audit is performed, identify any priority topics for coverage, and develop an employee interview schedule.

On-Site Audit Process An opening meeting with key facility personnel is held at which the audit team covers the objectives and approach for the audit, and the facility personnel provide an overview of the site operations including site safety rules and a site tour. The on-site audit process should then follow five basic steps that include: (1) understanding management systems, (2) evaluating management systems, (3) gathering audit information, (4) evaluating audit information, and (5) reporting audit findings (CCSP, 1993, p. 17).

An understanding of the management systems in place to control and direct the process safety of the facility can be obtained from reading engineering and administrative standards, guidelines, and procedures that should be available in the background information supplied

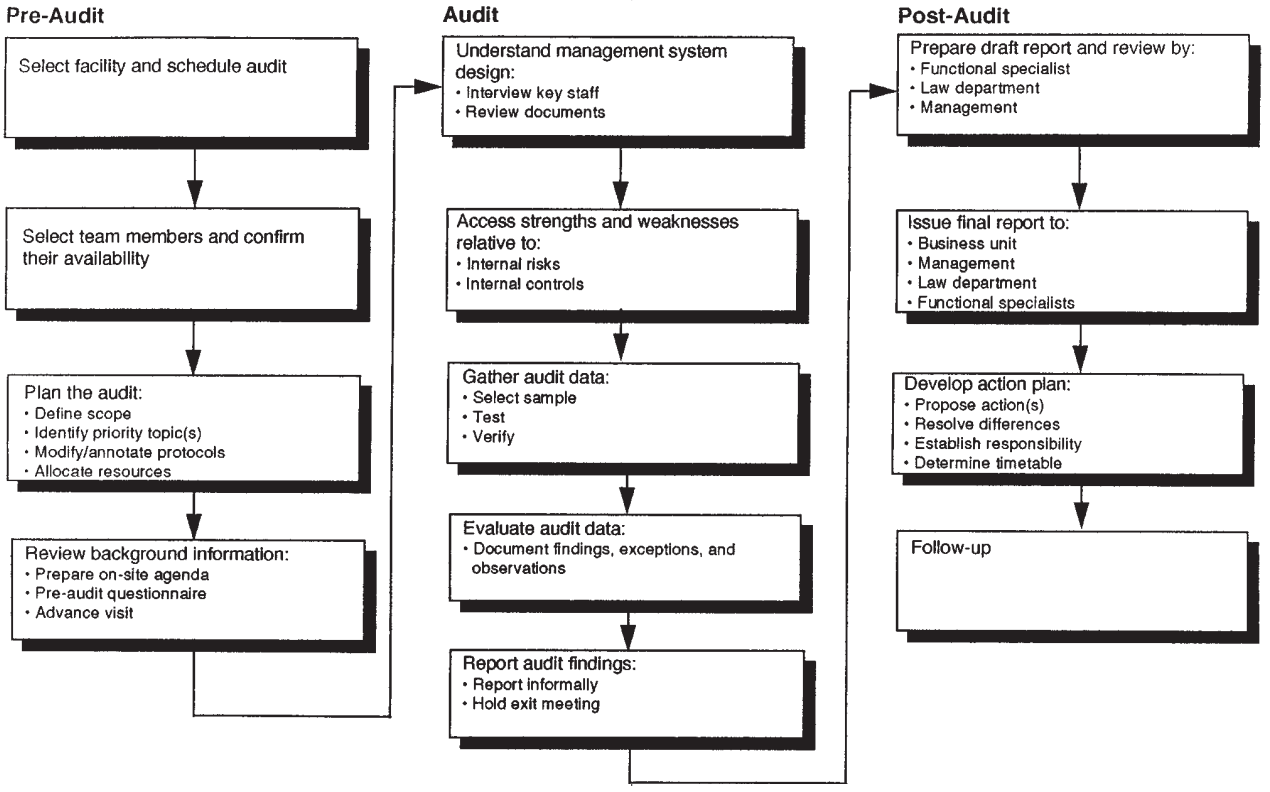


FIG. 26-12 Typical steps in the process safety management audit process. (*CCSP, 1993, by permission of AIChE.*)

prior to the on-site audit. Informal procedures and guidelines used by the facility may only be discovered in interviews with staff management and operations management. This understanding of the formal and informal management systems is a critical step in the audit process.

The next process step evaluates the process safety management systems to determine if they are adequate to achieve the desired results, and if they are used as intended. This evaluation is highly subjective on the auditor's part. This step sets the stage for the rest of the audit, guiding the auditor's information gathering and focusing attention on critical areas.

Gathering audit data can be accomplished through observations, documents, and interviews. The data obtained is used to verify and validate that the process safety management systems are implemented and functioning as designed. Data gathering can be aided by the use of audit samples, where a representative number of items are audited to draw a conclusion, and by using self-evaluation questionnaires.

The audit data can now be evaluated, resulting in audit findings (i.e., conclusions both positive and negative). The audit team should confirm that sufficient data has been collected to support each finding. Additional data may need to be gathered if the team decides a preliminary finding needs to be strengthened. The conclusions drawn from the data evaluation should be a team consensus.

The reporting step of the on-site audit should be planned to avoid any surprises to facility personnel. Reporting sessions should be held at the end of each audit day to inform facility personnel of the findings, clear up any misunderstandings of the data, and help redirect the audit team, if necessary. The on-site audit should end with a well-planned exit or closeout meeting between the audit team and facility personnel. All the findings of the audit team should be presented at this meeting. This verbal report is the opportunity for clarification of any ambiguities and determination of the final disposition of the findings (written audit report, for local attention only, etc.).

Postaudit Process The postaudit process consists of preparation of a draft report, preparation of a final report, development of action plans, and follow-up. A draft report of the audit findings should be prepared shortly after the completion of the on-site audit. The draft report usually undergoes review and comment by facility personnel involved with the audit, experienced auditors not involved with the subject audit, functional specialists, and attorneys. The review of the draft report is done to assure that a clear, concise, and accurate report is issued, and not to modify or change the findings. Once this review procedure is completed, a final report can be issued and distributed based on a distribution list provided by the facility personnel. The final audit report should be issued in a timely manner and meet the time requirement specified in the audit plan.

An action plan should be developed by the appropriate personnel of the audited facility to address any deficiencies stated in the audit report. Action plans should state what is to be done, who is responsible for getting it done, and when it is to be completed. Rationale for not taking any action for any of the stated deficiencies should also be documented. The action plan is an important step in closing the audit process.

It would not be unusual for some action plans to take a long time to complete. When extended implementation time is necessary, a follow-up mechanism should be used to document progress and show that an effort is being made to resolve the issues. Periodic (i.e., quarterly, semiannually) progress reports should be used as a follow-up method to ensure implementation. Future audits of the facility should include confirmation of the implementation of previous audit action plans.

The final audit report, action plans, progress reports, and any closure report should be retained by the facility based on the facility record retention policy. Typically, these items will be retained until future audit documentation replaces them. In some cases, audit records are retained for the life of the plant.

SAFETY DEVICES

PRESSURE RELIEF SYSTEMS

Nomenclature

C_p	Liquid heat capacity, Btu/lb-°F
Critical (or choked) condition	Maximum flow condition for compressible fluids
D	Duct diameter
F	Inlet mass flow rate, lb/min
f	Friction factor
G	Mass flux
g	Acceleration due to gravity
L	Flow length
M	Total mass in the equipment
P	Stream pressure
P_0	Stagnation pressure of the fluid (i.e., pressure under no-flow conditions)
P_1	Flowing pressure
Q	Heat input rate, Btu/min
R_v	Volume generation rate, ft³/min
t	Time
v	Specific volume of stream
v_f, v_g	Specific volumes of liquid and gas phases in the equipment
V_g, V_l	Specific volumes of gas and liquid phases, ft³/lb
V_r	Total equipment volume
W	Mass flow rate, lb/min
X_0	Quality, weight fraction vapor
X_r	Overall weight fraction vapor in the equipment
Greek letters	
β	Volumetric expansion coefficient, ft³/lb-°F
γ	C_p/C_v
ϕ	Angle of inclination from vertical
λ	Heat of vaporization, Btu/lb
ρ_f	Stream density entering the protected equipment, lb/ft³
ρ_w	Stream density entering the relief system, lb/ft³

Introduction All process designs should attempt to arrive at an inherently safe facility; that is, one from which a worst-case event cannot cause injury to personnel, damage to equipment, or harm to the environment. Incorporating safety features that are intrinsic (built-in) rather than extrinsic (added-on) to the basic design, together with the use of high-integrity equipment and piping, provide the first lines of defense against the dramatic, often catastrophic, effects of an overpressure and subsequent rupture. In recent years, many companies have incorporated the principles of *depressuring* or *instrumented shutdown* of key equipment as a means to control a release and avoid the actuation of pressure relief devices. This minimizes the probability of failure of the device, because, once used, the device may no longer be dependable. Since maintenance of relief devices can be sporadic, this redundancy provides yet another layer of safety. However, regardless of the number of lines of defense and depressuring systems in place, overpressure protection must still be provided. Emergency pressure relief systems are intended to provide the last line of protection and thus must be designed for high reliability, even though they will have to function infrequently.

Self-actuated pressure relief systems must be designed to limit the pressure rise which can occur as a result of overcompressing, overfilling, or overheating either an inert or a chemically reactive medium in a closed system. Pressure generation is usually the result of either expansion of a single-phase medium (by material addition and/or heating) or a shift of the phase equilibrium in a multiphase medium (as a result of composition and/or temperature changes). These mechanisms of pressure generation differ from what is commonly referred to as *explosion venting.* Events such as dust explosions and flammable vapor deflagrations propagate nonuniformly from a point of initiation, generating pressure or shock waves. Such venting problems are not included in these discussions.

Relief System Terminology Specific terminology has been developed for the various components which compose an emergency relief system. The American National Standards Institute (ANSI) definitions pertaining to relief devices themselves are listed as follows. Special care is required to avoid confusion on the following terms:

relief valve A pressure relief valve set up for liquid flow. This device opens gradually over a pressure range to avoid "hammer."

safety (pop) valve A pressure relief valve set up for gas or vapor flow. This device opens over a narrow pressure range, with an initial "pop" action.

safety relief valve A pressure relief valve with mechanical design or adjustments to allow either relief or safety service.

backpressure Pressure existing at the outlet of a relief device. The value under no-flow conditions is *superimposed* backpressure. The value under flowing conditions consists of both superimposed backpressure and built-up pressure due to piping pressure drop.

conventional vs. balanced valves In conventional valves, the downstream side of the closing mechanism is exposed to the backpressure of the flowing fluid; in balanced valves, the closing mechanism is isolated from the fluid and open to atmosphere.

set point The inlet gauge pressure at which a device will start to open (or a rupture disk will burst) under service conditions of temperature and backpressure.

differential set pressure The difference between the upstream and downstream pressures at the set point.

blowdown The reduction in flowing pressure below the set point required for a device to close.

overpressure The rise of inlet pressure above the set point during relief flow, usually expressed as a percentage of the differential set pressure.

maximum allowable working pressure (MAWP) The maximum allowed pressure at the top of the vessel in its normal operating position at the operating temperature specified for that pressure.

Accumulation The rise of pressure above the MAWP of the protected system, usually expressed as a percentage of the gauge MAWP. *Note:* The **MAWP** and **accumulation** terms are not included in the ANSI definitions since they relate to the protected system instead of the relief device.

Codes, Standards, and Guidelines Industry practice is to conform to the applicable regulations, codes, and recommended practices. In many cases, these will provide different guidelines. A suggested approach would be to review all applicable codes, standards, and recommended practices prior to choosing a design basis. In addition to currently available material, the Center for Chemical Process Safety (CCPS), formed by the American Institute of Chemical Engineers, is continually developing guidelines and conducting research to further the general knowledge in emergency relief system design. The Design Institute for Emergency Relief Systems (DIERS) was established by AIChE to address sizing aspects of relief systems for two-phase, vapor-liquid flashing flow regimes. The DIERS Project Manual (Emergency Relief System Design Using DIERS Technology—1992) is the generally accepted industry standard for two-phase relief venting.

NFPA 30 and API Standard 2000 provide guidance for design of overpressure protection involving storage tanks that operate at or near atmospheric pressure. In particular, NFPA 30 focuses on flammability issues, while API 2000 addresses both pressure and vacuum requirements. The ASME code (Sections I and VIII) and API RP 520 are the primary references for pressure relief device sizing requirements.

Designers of emergency pressure relief systems should be familiar with the following list of regulations, codes of practice, and industry standards and guidelines.

API RP 520. *Sizing, Selection, and Installation of Pressure-Relieving Devices in Refineries.* Part I, Sizing and Selection, 5th ed., July 1990, and Part II, Installation, 3d ed., November 1988. American Petroleum Institute, Washington, D.C.

API RP 521. 1990. *Guide for Pressure-Relieving and Depressuring Systems,* 3d ed., American Petroleum Institute, Washington, D.C.

API STD 2000. 1992. *Venting Atmospheric and Low-Pressure Storage Tanks, Nonrefrigerated and Refrigerated.* American Petroleum Institute, Washington, D.C.

API RP 2001. 1984. *Fire Protection in Refineries.* American Petroleum Institute, Washington, D.C.

ASME. 1992. *Boiler and Pressure Vessel Code,* Section I, Power Boilers, and Section VIII, Pressure Vessels. American Society of Mechanical Engineers, New York.

ASME. 1988. *Performance Test Code PTC-25, Safety and Relief Valves.* American Society of Mechanical Engineers, New York.

CCPS. 1993. *Engineering Design for Process Safety.* American Institute of Chemical Engineers, New York.

DIERS. 1992. *Emergency Relief System Design Using DIERS Technology, DIERS Project Manual.* American Institute of Chemical Engineers, New York.

National Board of Boiler and Pressure Vessel Inspectors. 1992. *Pressure Relieving Device Certification (Red Book),* National Board of Boiler and Pressure Vessel Inspectors, Columbus, Ohio.

NFPA 30. 1990. *Flammable and Combustible Liquids Code.* National Fire Protection Association, Quincy, Mass.

Relief Design Scenarios The most difficult part of designing an adequate emergency pressure relief system is determining the emergency events (credible design scenarios) for which to design. The difficulty arises primarily because the identification of credible design scenarios usually involves highly subjective judgments, which are often influenced by economic situations. Unfortunately, there exists no universally accepted list of credible design scenarios. Relief systems must be designed for the credible chain of events that results in the most severe venting requirements (worst credible scenario). Credibility is judged primarily by the number and the time frame of causative failures required to generate the postulated emergency. Only totally independent equipment or human failures should be considered when judging credibility. A failure resulting from another failure is an effect, rather than an independent causative factor. A suggested guideline for assessing credibility as a function of the number and time frames of independent causative events is:

- Any single failure is *credible.*
- Two or more simultaneous failures are *not credible*
- Two events in sequence are *credible.*
- Three or more events in sequence are *not credible.*

The first step in scenario selection is to identify all the credible emergencies using the preceding guidelines (or a similar set). This is perhaps best accomplished by identifying all the possible sources of pressure and vacuum. Table 26-7 lists a number of commonly existing pressure and vacuum sources.

Fire The main consequence of fire exposure is heat input causing thermal expansion, vaporization, or thermally induced decomposition resulting in a pressure rise. An additional result of fire exposure is the possibility of overheating the wall of the equipment in the vapor space where the wall is not cooled by the liquid. In this case, the vessel wall may fail due to the high temperature, even though the relief system is operating. Guidelines for estimating the heat input from a fire are found in API recommended practices, NFPA 30 (for bulk storage tanks), OSHA 1910.106, and corporate engineering standards. In determining the heat input from fire exposure, NFPA allows credit for application of water spray to a vessel; API allows no such credit.

Pressure vessels (including heat exchangers and air coolers) in a plant handling flammable fluids are subject to potential exposure to external fire. A vessel or group of vessels which could be exposed to a pool fire must be protected by a pressure relief device. Additional protection to reduce the device relief load can be provided by insulation, water spray, or remote-controlled depressuring devices. Plant layout should consider spacing requirements, such as those set forth by NFPA, API, Industrial Risk Insurers, or Factory Mutual, and must include accessibility for fire-fighting personnel and equipment. Several pieces of equipment located adjacent to each other that cannot be isolated by shutoff valves can be protected by a common relief device, providing the interconnecting piping is large enough to handle the required relief load.

TABLE 26-7 Common Sources of Pressure and Vacuum

Heat Related
• Fire
• Out-of-control heaters and coolers
• Ambient temperature changes
• Runaway chemical reactions
Equipment and Systems
• Pumps and compressors
• Heaters and coolers
• Vaporizers and condensers
• Vent manifold interconnections
• Utility headers (steam, air, water, etc.)
Physical Changes
• Gas absorption (e.g., HCl in water)
• Thermal expansion
• Vapor condensation

Operational Failures A number of scenarios of various operational failures may result in the generation of overpressure conditions:

- *Blocked outlet.* Operation or maintenance errors (especially following a plant turnaround) can block the outlet of a liquid or vapor stream from a piece of process equipment, resulting in an overpressure condition.
- *Opening a manual valve.* Manual valves which are normally closed to isolate two or more pieces of equipment or process streams can be inadvertently opened, causing the release of a high-pressure stream or resulting in vacuum conditions. Other effects may include the development of critical flows, flashing of liquids, or the generation of a runaway chemical reaction.
- *Cooling water failure.* The loss of cooling water is one of the more commonly encountered causes of overpressurization. Two examples of the critical consequences of this event are the loss of condensing duty in column overhead systems and the loss of cooling for compressor seals and lube oil systems. Different scenarios should be considered for this event, depending on whether the failure affects a single piece of equipment (or process unit) or is plantwide.
- *Power failure.* The loss of power will shut down all motor-driven rotating equipment, including pumps, compressors, air coolers, and vessel agitators. As with cooling water failure, power failure can have a negative cascading effect on other equipment and systems throughout the plant.
- *Instrument air failure.* The consequences of the loss of instrument air should be evaluated in conjunction with the failure mode of the control valve actuators. It should not be assumed that the correct air failure response will occur on these control valves, as some valves may stick in their last operating position.
- *Thermal expansion.* Equipment and pipelines which are liquid-full under normal operating conditions are subject to hydraulic expansion if the temperature increases. Common sources of heat that can result in high pressures due to thermal expansion include solar radiation, steam or other heated tracing, heating coils, and heat transfer from other pieces of equipment.
- *Vacuum.* Vacuum conditions in process equipment can develop due to a wide variety of situations including:

Instrument malfunction

Draining or removing liquid with venting

Shutting off purge steam without pressuring with noncondensable vapors

Extreme cold ambient temperatures resulting in subatmospheric vapor pressures

Water addition to vessels that have been steam-purged

If vacuum conditions can develop, then either the equipment must be designed for vacuum conditions or a vacuum relief system must be installed.

Equipment Failure Most equipment failures that can lead to overpressure situations involve the rupture or break of internal tubes inside heat exchangers and other vessels and the failure of valves and regulators. Heat exchangers and other vessels should be protected with a relief system of sufficient capacity to avoid overpressure in case of internal failure. Characterization of the types of failure and the design of the relief system are left to the discretion of the designer. API RP 520 presents guidance in determining these requirements, including criteria for deciding when a full tube rupture is likely. In cases involving the failure of control valves and regulators, it is important to evaluate both the fail-open and fail-closed positions.

Runaway Reactions Runaway temperature and pressure in process vessels can occur as a result of many factors, including loss of cooling, feed or quench failure, excessive feed rates or temperatures, contaminants, catalyst problems, and agitation failure. Of major concern is the high rate of energy release and/or formation of gaseous products, which may cause a rapid pressure rise in the equipment. In order to properly assess these effects, the reaction kinetics must either be known or obtained experimentally.

Pressure Relief Devices The most common method of overpressure protection is through the use of safety relief valves and/or rupture disks which discharge into a containment vessel, a disposal system, or directly to the atmosphere (Fig. 26-13). Table 26-8 summarizes some of the device characteristics and the advantages.

Safety Relief Valves *Conventional* safety relief valves (Fig. 26-14) are used in systems where built-up backpressures typically do not exceed 10 percent of the set pressure. The spring setting of the valve is reduced by the amount of superimposed backpressure expected. Higher built-up backpressures can result in a complete loss of continuous valve capacity. The designer must examine the effects of other relieving devices connected to a common header on the performance of each valve. Some mechanical considerations of conventional relief valves are presented in the ASME code; however, the manufacturer should be consulted for specific details.

Balanced safety relief valves may be used in systems where built-up and/or superimposed backpressure is high or variable. In general, the capacity of a balanced valve is not significantly affected by backpressures below 30 percent of set pressure. Most manufacturers recommend keeping the backpressure on balanced valves below 45 to 50 percent of the set pressure.

Pilot-Operated Relief Valves In a pilot-operated relief valve, the main valve is combined with and controlled by a smaller, self-actuating pressure relief valve. The pilot is a spring-loaded valve that senses the process pressure and opens the main valve by lowering the pressure on the top of an unbalanced piston, diaphragm, or bellows of the main valve. Once the process pressure is lowered to the blowdown pressure, the pilot closes the main valve by permitting the pressure in the top of the main valve to increase. Pilot-operated relief valves are commonly used in clean, low-pressure services and in services where a large relieving area at high set pressures is required. The set pressure of this type of valve can be close to the operating pressure. Pilot-operated valves are frequently chosen when operating pressures are within 5 percent of set pressures and a close tolerance valve is required.

TABLE 26-8 Summary of Device Characteristics

	Reclosing devices		Nonreclosing devices
	Relief valves	Disk-valve combinations	Rupture disks
Fluid above normal boiling point	+	+	–
Toxic fluids	+	+	–
Corrosive fluids	–	+	+
Cost	–	–	+
Minimum pipe size	–	–	+
Testing and maintenance	–	–	+
Won't fatigue and fail low	+	+	–
Opens quickly and fully	–	–	+

NOTE: + indicates advantageous
– indicates disadvantageous

Rupture Disks A rupture disk is a device designed to function by the bursting of a pressure-retaining disk (Fig. 26-15). This assembly consists of a thin, circular membrane usually made of metal, plastic, or graphite that is firmly clamped in a disk holder. When the process reaches the bursting pressure of the disk, the disk ruptures and releases the pressure. Rupture disks can be installed alone or in combination with other types of devices. Once blown, rupture disks do not reseat; thus, the entire contents of the upstream process equipment will be vented. Rupture disks are commonly used in series (upstream) with a relief valve to prevent corrosive fluids from contacting the metal parts of the valve. In addition, this combination is a reclosing system.

The burst tolerances of rupture disks are typically about ±5 percent for set pressures above 40 psig.

Pressure-Vacuum Relief Valves For applications involving atmospheric and low-pressure storage tanks, pressure-vacuum relief valves (PVRVs) are used to provide pressure relief. These units combine both a pressure and a vacuum relief valve into a single assembly that mounts on a nozzle on top of the tank and are usually sized to handle the normal in-breathing and out-breathing requirements. For emergency pressure relief situations (e.g., fire), ERVs are used. API RP 520 and API STD 2000 can be used as references for sizing.

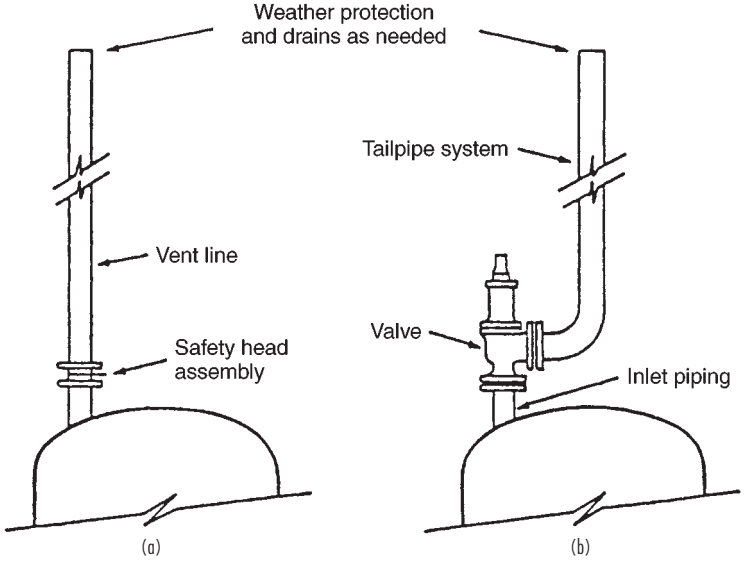


FIG. 26-13 Typical pressure relief system configurations: (*a*) rupture disk system; (*b*) pressure relief valve system.

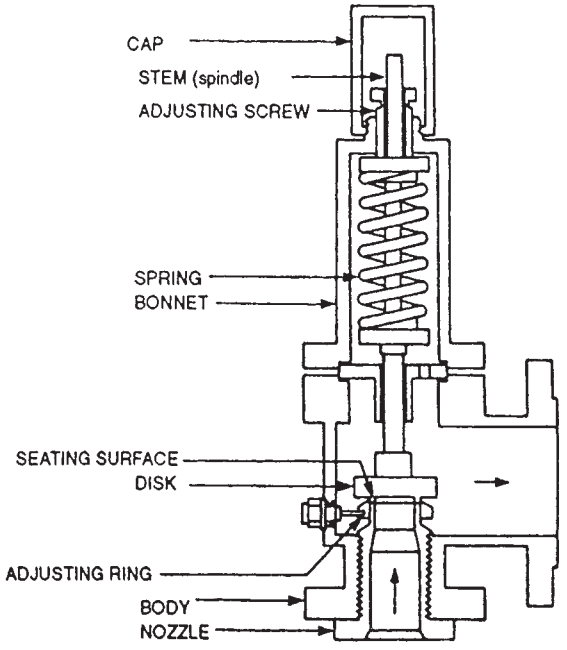


FIG. 26-14 Typical conventional pressure relief valve.

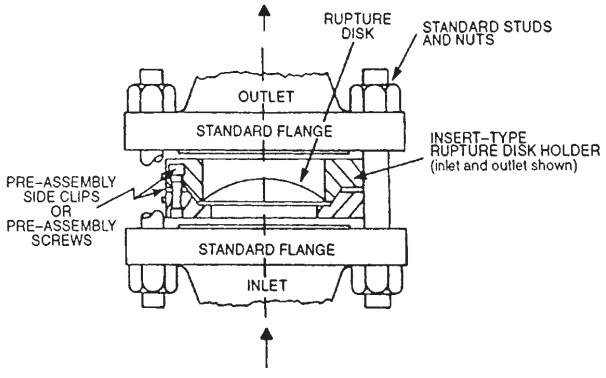


FIG. 26-15 Typical rupture disk assembly.

Sizing of Pressure Relief Systems A critical point in design is determining whether or not the relief system must be sized for single-phase or two-phase relief flow. Two-phase flow frequently occurs during a runaway reaction, but it can also occur in nonreactive systems such as vessels with gas-spargers, vessels experiencing high heat input rates, or systems containing known foaming agents such as latex. In 1976, the Design Institute for Emergency Relief Systems (DIERS) was formed to develop methods for the design of emergency relief systems to handle runaway reactions. The DIERS group consisted of a consortium of 29 companies under the auspices of the American Institute of Chemical Engineers. Of particular interest were the prediction of when two-phase flow venting would occur and the applicability of various sizing methods for two-phase vapor-liquid flashing flow situations. The most significant theoretical and experimental finding of the DIERS program is the ease with which two-phase vapor-liquid flow can occur during an emergency relief situation and the requirement for a much larger (by two to ten times) relief system. The DIERS methodology is important as a means of addressing situations, such as two-phase flow, not covered adequately by ASME and API methods. The *DIERS Project Manual* (DIERS, 1992) is the best source of detailed information on these methods.

Required Relief Rate The required relief rate is the venting rate required to remove the volume being generated within the protected equipment when the equipment is at its highest allowed pressure:

$$W_{\text{required}} = \frac{\text{net volume generation rate}}{\text{specific volume of vent stream}} \tag{26-21}$$

The required relief rate is constant only if both the numerator and denominator in Eq. (26-21) are constant. If the conditions within the protected equipment (temperature, composition, etc.) or the composition and/or quality of the vent stream are changing, then the required relief rate as defined above represents the instantaneous required relief rate. For steady-state design scenarios, the required relief rate, once determined, provides the capacity information that is required to properly size the relief device and associated piping. For situations that are transient in nature (e.g., the venting of a vessel exposed to fire), the required relief rate will be continually changing as the equipment is emptied. In these situations the design should be done based on finding the required vent area that will keep the pressure in the protected equipment at (or below) the maximum allowed accumulation during the entire venting period. These cases will require the simultaneous solution of the applicable material and energy balances around the protected equipment.

Constant Flow into Protected Equipment For the steady-state design scenario with a constant, steady flow of fluid from a pressure source that is above the maximum allowed pressure in the protected equipment, volume is being generated within the equipment at a rate $RV = F/\rho_f$. Substituting into Eq. (26-21) and noting that the specific volume of the vent stream is $1/\rho_w$ gives the required mass flow rate:

$$W = \frac{F\rho_w}{\rho_f} \tag{26-22}$$

where W = required mass flow rate, lb/min
F = inlet mass flow rate, lb/min
ρ_w = stream density entering the relief system, lb/ft^3
ρ_f = stream density entering the protected equipment, lb/ft^3

Constant Energy Input into Protected Equipment If the design scenario involves a constant flow of energy (heat) into the protected equipment, then the required flow rate calculation involves determining whether or not a phase change (boiling) is occurring. If the addition of heat to the equipment does not cause the fluid to boil, then the volume generation rate is the thermal expansion rate of the fluid:

$$R_v = \frac{\beta Q}{C_p} \tag{26-23}$$

where R_v = volume generation rate, ft^3/min
β = volumetric expansion coefficient, ft^3/lb-°F
Q = heat input rate, Btu/min
C_p = liquid heat capacity, Btu/lb-°F

Combining Eqs. (26-23) and (26-22) gives the required relief rate:

$$W = \frac{\rho_w \beta Q}{C_p} \tag{26-24}$$

If the fluid is at its boiling point, then volume is generated through the phase change that occurs upon vaporization:

$$R_v = \frac{[Q(V_g - V_l)]}{\lambda} \tag{26-25}$$

where V_g, V_l = specific volumes of gas and liquid phases, ft^3/lb
λ = heat of vaporization, Btu/lb

As before, the required relief rate becomes:

$$W = \frac{[\rho_w Q(V_g - V_l)]}{\lambda} \tag{26-26}$$

Transient Material and Energy Balances The relief rate requirement at any instant during any event is developed on the basis that the total volume of vapor plus liquid is just equal to the vessel vol-

ume. In differential form, this condition is equivalent to setting the volumetric vent rate equal to the rate of volume increase in the protected equipment at any instant. The development of the relief rate criterion, which relates the rate of vapor generation to the venting rate, is based on the assumption that the equipment geometry is such that the temperature and pressure will be reasonably uniform throughout the contents, with negligible composition gradients within the phases. In addition, the time scale of the relief event is assumed to be small enough that influence of any feed streams is insignificant relative to the venting stream. Under these assumptions the material balance around the protected equipment is given by:

$$\frac{dX_r}{dt} = \frac{\left(\frac{WV_r}{M^2} - (1 - X_r)\frac{dv_f}{dt} - X_r\frac{dv_g}{dt}\right)}{v_g - v_f} \qquad (26\text{-}27)$$

where V_r = total equipment volume
X_r = overall weight fraction vapor in the equipment
M = total mass in the equipment
v_f, v_g = specific volumes of liquid and gas phases in the equipment
W = mass vent rate
t = time

The energy balance on the equipment is developed for conditions under which thermal mixing within the vessel is sufficient to allow the properties of all portions of the liquid and vapor phases to be characterized adequately by a single value of temperature. It is assumed also that pressure gradients within the vessel are small with respect to the pressure level so that a single value of pressure may be assigned to the contents. The resulting expression for the incompressible liquid–ideal gas case is given by Huff ("Emergency Venting Requirements," *Plant/Operations Progress,* October 1982, p. 212):

$$\frac{dT}{dt}\left[X_r(C_{pg} - R) + (1 - X_r)\left(C_{pf} - T\frac{dv_f}{dT}\frac{dP}{dT}\right)\right]$$
$$= Q - [\lambda - P(v_g - v_f)]\frac{dX_r}{dt} - \frac{W}{M}\{[X_0 - X_r][\lambda - P(v_g - v_f)] + P[X_0 v_g + (1 - X_0)v_f]\} \qquad (26\text{-}28)$$

where T and P are the temperature and pressure of the contents, C_{pg} and C_{pf} are the gas and liquid specific heats, λ is the latent heat of vaporization, R is the universal gas constant, and Q is the rate of heat addition to the equipment contents. The solution of Eq. (26-28) requires a value of the quality of the vent stream as it leaves the protected equipment (X_0). Limiting cases are $X_0 = 1$ (all-vapor venting) and $X_0 = 0$ (all-liquid venting). If the venting process is such that no vapor-liquid disengagement occurs, then the criterion for top venting becomes $X_0 = X_r$, where X_r is the mass fraction vapor in the equipment.

The time-dependent nature of the emergency pressure relieving event is obtained by the simultaneous solution of Eqs. (26-27) and (26-28). Generally, the only unknown parameters in these two equations are the venting rate W and the vent stream quality (X_0). The vent rate W at any instant is a function of the upstream conditions and the relief system geometry.

Vessel Flow Models and the Coupling Equation In order to evaluate the quantity of vapor entering the vent system at any instant (X_0), one must consider the dynamics of vapor disengagement that occur in the top of the protected equipment. Based on experience gained in the DIERS program, a number of vapor-liquid disengagement models have been formulated. These models estimate the liquid swell (i.e., the degree of vapor-liquid disengagement) as a function of vapor throughput. The key model parameters include the average void fraction in the swelled liquid, the vapor superficial velocity at the liquid surface, and the characteristic bubble rise velocity. The vessel flow models used in the DIERS program are listed as follows in order of increasing vapor-liquid disengagement.

Homogeneous Vessel Model This model assumes that no vapor-liquid disengagement occurs in the protected equipment; thus, the vapor mass fraction entering the vent system (X_0) will be the same as the average vapor mass fraction in the equipment (X_r). This model is used to approximate the vessel conditions when the vessel contents are extremely viscous or foamy. The specification $X_0 = X_r$ has come into rather wide use as a conservative but realistic basis for taking account of the two-phase venting phenomena.

Bubbly Vessel Model The bubbly vessel model assumes uniform vapor generation throughout the liquid with limited disengagement in the vessel. In this model, the liquid phase is continuous with discrete bubbles.

Churn-Turbulent Vessel Model The churn-turbulent vessel model is also based on uniform vapor generation throughout the liquid but with considerable vapor-liquid disengagement. The liquid phase is continuous with coalesced vapor regions of increased size relative to the bubble vessel model.

Nonboiling Height Model This model applies the churn-turbulent assumptions to only a top portion of the fluid in the protected equipment. Below this portion, boiling does not occur and there is no liquid swell. The location of this nonboiling height is estimated from a balance of the hydrostatic effects and the recirculation effects.

The coupling equation is a vapor mass balance written at the vent system entrance and provides a relationship between the vent rate W and the vent system inlet quality X_0. The relief system flow models described in the following section provide a second relationship between W and X_0 to be solved simultaneously with the coupling equation. Once W and X_0 are known, the simultaneous solution of the material and energy balances can be accomplished. For all the preceding vessel flow models and the coupling equations, the reader is referred to the *DIERS Project Manual* for a more complete and detailed review.

Vent System Flow Capacity The mass flow rate W through a given vent system geometry, in general, requires a trial-and-error approach when the system configuration contains more than a single diameter. The generalized approach is to assume a flow rate W and calculate the resulting pressure profiles down the system until the final discharge pressure matches the specified value. If choked flow is encountered at any point in the system, then the system must be broken into two or more separate systems and each treated independently while preserving the mass flow rate through each.

The presence of both liquid and vapor phases in the vent stream is normally treated as a vapor-liquid mixture at equilibrium conditions. The adiabatic flashing of the stream as the pressure falls along the flow path is usually computed by conventional flash distillation methods. In principle, the flash path should be isentropic for flow in devices exhibiting low friction losses (nozzles and short pipes). For friction flow, the sum of the stream enthalpy, kinetic energy, and potential energy is held constant along the path. In practice, little error is introduced by carrying out the flash computations at constant enthalpy. With this simplification, the flash temperature-pressure-composition history can be established before starting the actual flow calculations, thus eliminating the need for repetitive flash calculations at each step in the integration.

The treatment of vent flow calculations in most typical relief system configurations involves two classes of computational models: flow in low-friction geometries such as nozzles and frictional flow in pipes and fittings.

Ideal (Frictionless) Flow in Nozzles The flow path in well-formed nozzles follows smoothly along the nozzle contour without separating from the wall. The effects of small imperfections and small frictional losses are accounted for by correcting the ideal nozzle flow by an empirically determined coefficient of discharge. The acceleration of a fluid initially at rest to flowing conditions in an ideal nozzle is given by:

$$-\frac{G^2 v^2}{2} = \int_{P_0}^{P_1} v\, dP \qquad (26\text{-}29)$$

where P_0 is the stagnation pressure of the fluid (i.e., the pressure under no-flow conditions), P_1 is the flowing pressure, G is the mass flux, and v is the fluid specific volume. If the fluid is compressible, the flow will increase to a maximum value as the downstream pressure P_1 is reduced and any further decrease in the downstream pressure will not affect the flow. This maximum flow condition is referred to as the

critical (or *choked*) condition. At this condition, the maximum mass flux is

$$G_{max} = \sqrt{\frac{-1}{dv/dp}} \qquad (26\text{-}30)$$

Pipe Flow For steady-state flow through a constant diameter duct, the mass flux G is constant and the governing steady-state momentum balance is:

$$vdP + G^2\left[vdv + \left(\frac{4fv^2}{2D}\right)dL\right] + g\cos\phi dL = 0 \qquad (26\text{-}31)$$

where G = mass flux
v = specific volume of stream
P = stream pressure
f = friction factor
D = duct diameter
L = flow length
g = acceleration due to gravity
ϕ = angle of inclination from vertical

Equation (26-31) can be integrated directly to yield the mass flux G, provided that D, L, f, and ϕ are known, as well as the relationship between pressure and volume. For all-vapor cases, the expansion of the vapor is usually assumed to follow the form Pv^γ = constant ($\gamma = C_p/C_v$) and thus the momentum equation can be analytically integrated. Similarly, for all-liquid (nonflashing) flow, the stream specific volume is usually assumed to be constant, thus also providing a direct analytical integration of Eq. (26-31). For two-phase flashing flow, the requisite p-v relationship is usually obtained from flash calculations, and normally requires a numerical integration of Eq. (26-31). In addition to calculating the flow rates through sections of piping in the relief system, there may also exist additional pressure drop constraints in both the inlet and outlet piping if the relief device is a PRV. The designer is referred to the ASME and API references for further information.

A number of papers have explored methods for the solution of Eqs. (26-29) and (26-31), especially for the two-phase conditions. The reader is referred to the *DIERS Project Manual* for a more detailed review and list of appropriate references and available computer programs.

EMERGENCY RELIEF DEVICE EFFLUENT COLLECTION AND HANDLING

Nomenclature (consistent English or SI units)

A_v	Vapor flow area, ft^2
C_q	Specific heat of the quench fluid
C_R	Specific heat of the reactants
D	Drum diameter, ft
G_v	Superficial vapor mass flux, lb/s · ft^2
k	Capacity coefficient
L	Drum length, ft
M	Molecular weight of vapor
m_o	Mass of reactants
P	Pressure in the drum, psia
Q_v	Vapor flow rate, ft^3/s
r	Volumetric vapor flow rate/volumetric liquid flow rate
T	Temperature of the vapor, °R
T_a	Allowable temperature following complete quench
T_o	Initial temperature of the quench fluid
T_R	Temperature of reactants at relief set pressure
U_a	Allowable vapor velocity, ft/s
V_L	Drum liquid volume, ft^3
V_v	Superficial velocity, ft/s
W	Vapor flow rate, lb/h
	Greek letters
ρ_L	Liquid density, lb/ft^3
ρ_v	Vapor density, lb/ft^3

General References: API Report 521, *Guide for Pressure Relieving and Depressurizing Systems,* American Petroleum Institute, Washington, D.C., March 1997. AIChE-CCPS, *Guidelines for Pressure Relief and Effluent Handling Systems,* AIChE, New York, 1997. DIERS, *Emergency Relief System Design Using DIERS Technology,* AIChE, New York, 1992. Fthenakis, *Prevention and Control of Accidental Releases of Hazardous Gases,* Van Nostrand-Reinhold, New York, 1993. Grossel and Crowl, *Handbook of Highly Toxic Materials Handling and Management,* Marcel Dekker, New York, 1995. Grossel, *Journal of Loss Prevention in the Process Industries* **3**(1): 112–124, 1990. Grossel, *Plant/Operations Progress* **5**(3): 129–135, 1986. Keiter, A. G., *Plant/Operations Progress* **11**(3): 157–163, 1992.

Introduction In determining the disposal of an effluent vent stream from an emergency relief device (safety valve or rupture disk), a number of factors must be considered, such as:

1. Is the stream single-phase (gas or vapor) or multiphase (vapor-liquid or vapor-liquid-solid)?
2. Is the stream flammable or prone to deflagration?
3. Is the stream toxic?
4. Is the stream corrosive to equipment or personnel?

Some vent streams, such as light hydrocarbons, can be discharged directly to the atmosphere even though they are flammable and explosive. This can be done because the high-velocity discharge entrains sufficient air to lower the hydrocarbon concentration below the lower explosive limit (API RP 521, 1997). Toxic vapors must be sent to a flare or scrubber to render them harmless. Multiphase streams, such as those discharged as a result of a runaway reaction, for example, must first be routed to separation or containment equipment before final discharge to a flare or scrubber.

These matters are organized into three major divisions: the types of equipment, the criteria employed in the selection of equipment, and the sizing and design of the equipment.

Types of Equipment The three most commonly used types of equipment for handling emergency relief device effluents are *blowdown drums* (also called *knockout drums* or *catch tanks*), *cyclone vapor-liquid separators,* and *quench tanks* (also called *passive scrubbers*). These are described as follows.

Horizontal Blowdown Drum/Catch Tank This type of drum, shown in Fig. 26-16, combines both the vapor-liquid separation and holdup functions in one vessel. Horizontal drums are commonly used where space is plentiful, such as in petroleum refineries and petrochemical plants. The two-phase mixture usually enters at one end and the vapor exits at the other end. For two-phase streams with very high vapor flow rates, inlets may be provided at each end, with the vapor outlet at the center of the drum, thus minimizing vapor velocities at the inlet and aiding vapor-liquid separation.

Cyclone Separator with Separate Catch Tank This type of blowdown system, shown in Fig. 26-17 and 26-18, is frequently used in chemical plants where plot plan space is limited. The cyclone performs the vapor-liquid separation, while the catch tank accumulates the liquid from the cyclone. This arrangement allows location of the cyclone knockout drum close to the reactor so that the length of the relief device discharge line can be minimized. The cyclone has internals, vital to its proper operation, which will be discussed in the following sections.

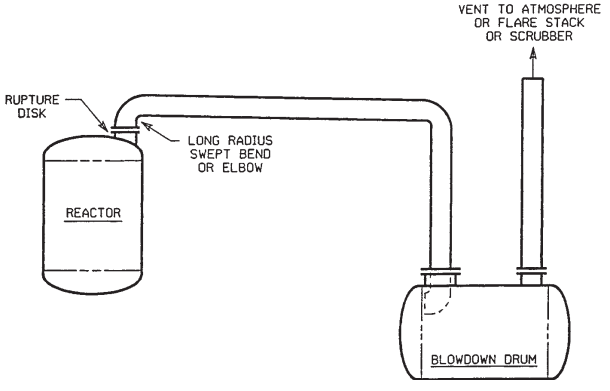


FIG. 26-16 Horizontal blowdown drum.

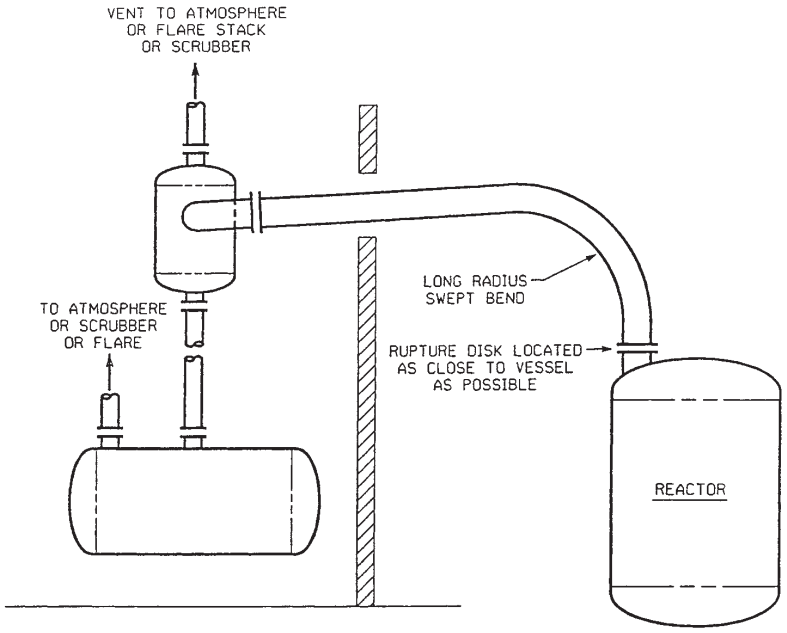


FIG. 26-17 Cyclone separator with separate liquid catch tank.

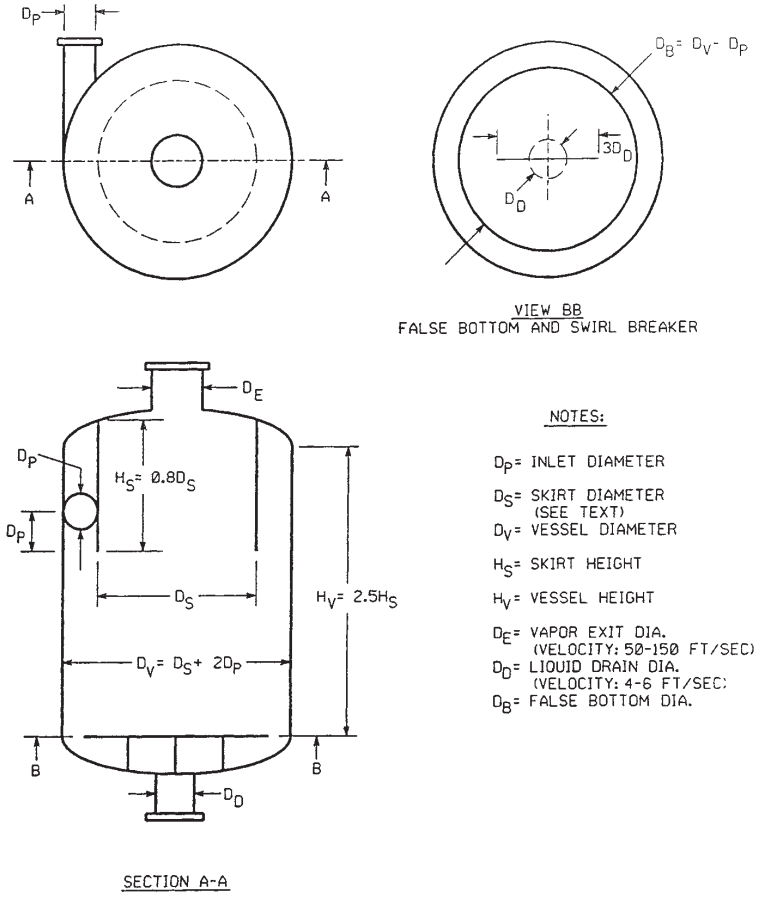


FIG. 26-18 Cyclone separator design details.

Cyclone Separator with Integral Catch Tank This type of containment system, depicted in Fig. 26-19, is similar to the aforementioned type, except that the knockout drum and catch tank are combined in one vessel shell. This design is used when the vapor rate is quite high so that the knockout drum diameter is large.

Quench Tank/Catch Tank This type of system, as shown in Figs. 26-20 and 26-21, is used when it is desired to remove condensable vapors from a flammable or toxic vent mixture by passing them through a pool of liquid in a vessel. This arrangement often obviates the need for a subsequent scrubber and/or flare stack. The design of the quencher arm is critical to efficient condensation and avoidance of water hammer. Figure 26-20 is the more conventional passive-type quenching pool used in the chemical and nuclear industry. The type shown in Fig. 26-21, with a superimposed baffle-plate section, is used when complete condensation of the incoming vapors is not expected. The exiting vapors are usually cooled to 150 to 200°F in the baffle plate section. This type is often used in petroleum refineries.

Multireactor Knockout Drum/Catch Tank This interesting system, depicted in Fig. 26-22, is sometimes used as the containment vessel for a series of closely spaced reactors (Speechly et al., "Principles of Total Containment System Design," presented at *I. Chem. E North West Branch Meeting,* 1979). By locating the drum as shown in Fig. 26-22, minimum-length vent lines can be routed directly to the vessel without any bends.

Equipment Selection Criteria and Guidelines A number of factors should be considered in order to determine when to select a blowdown drum, cyclone separator, or quench tank to handle a multiphase stream from a relief device. Among these are the plot plan space available, the operating limitations of each type, and the physicochemical properties of the stream.

The criteria for application and performance characteristics of blowdown drums, cyclone separators, and quench tanks are discussed as follows.

Horizontal Blowdown Drums (Catch Tanks)

Applications:

1. Inlet liquid loading is greater than 20 wt % based on gas flow rate.
2. They can be used for viscous and/or fouling service.

Performance Characteristics:

1. Residual entrainment is in the range of tenths to a few percent.
2. Pressure drop is usually very low.
3. Efficiency of separation is weakly dependent on the size of the vessel.
4. They are usually able to separate droplets 300 μm and larger.

Cyclones

Applications:

1. They can handle liquids with low to moderate viscosity.
2. Some fouling is acceptable.
3. Inlet liquid loading is generally less than 20 wt % based on the gas flow rate, but higher loadings are sometimes possible.

Performance Characteristics:

1. They have higher separation efficiency than a horizontal knockout drum.
2. Pressure drop is higher than that of a horizontal knockout drum.

Quench Tanks

Applications:

1. They can handle liquids with low to high viscosity.
2. They can handle liquids with moderate solids loading.
3. They can handle high liquid loading—actually no limit, as vessel can be sized to contain all the liquid.

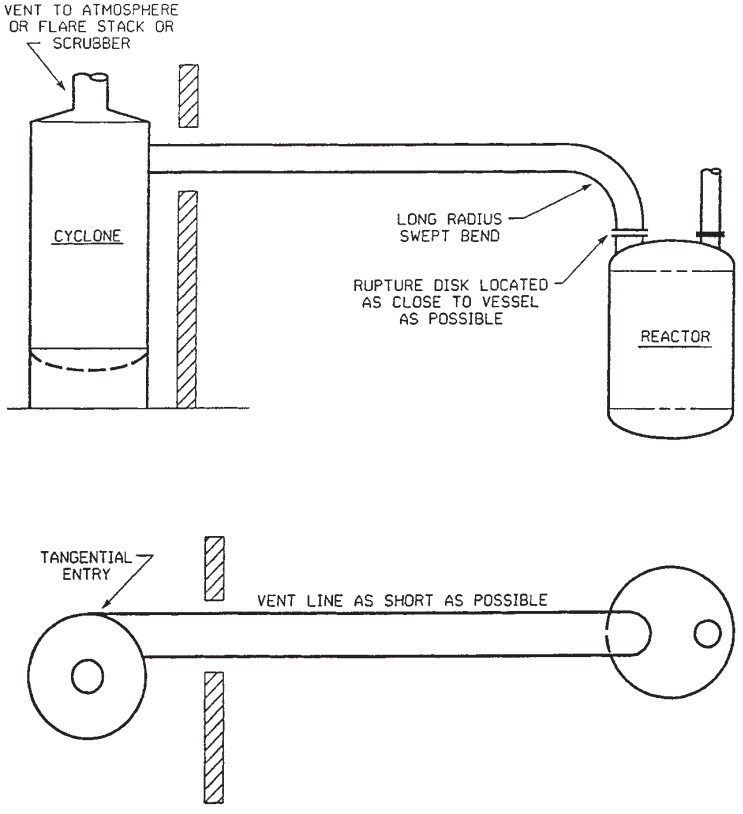


FIG. 26-19 Cyclone separator with integral catch tank.

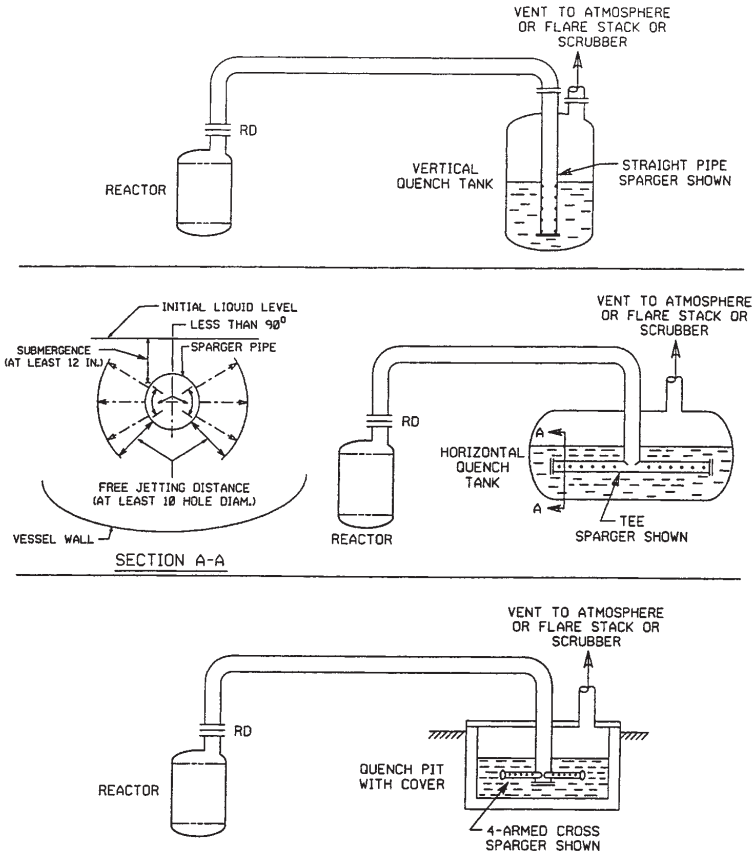


FIG. 26-20 Quench tank/catch tank.

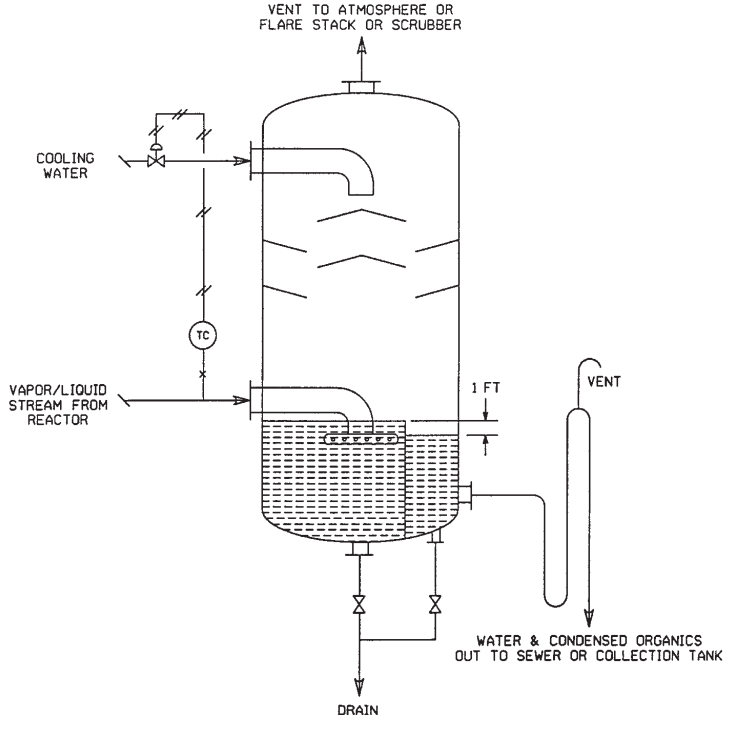


FIG. 26-21 Quench tank with direct-contact baffle tray section.

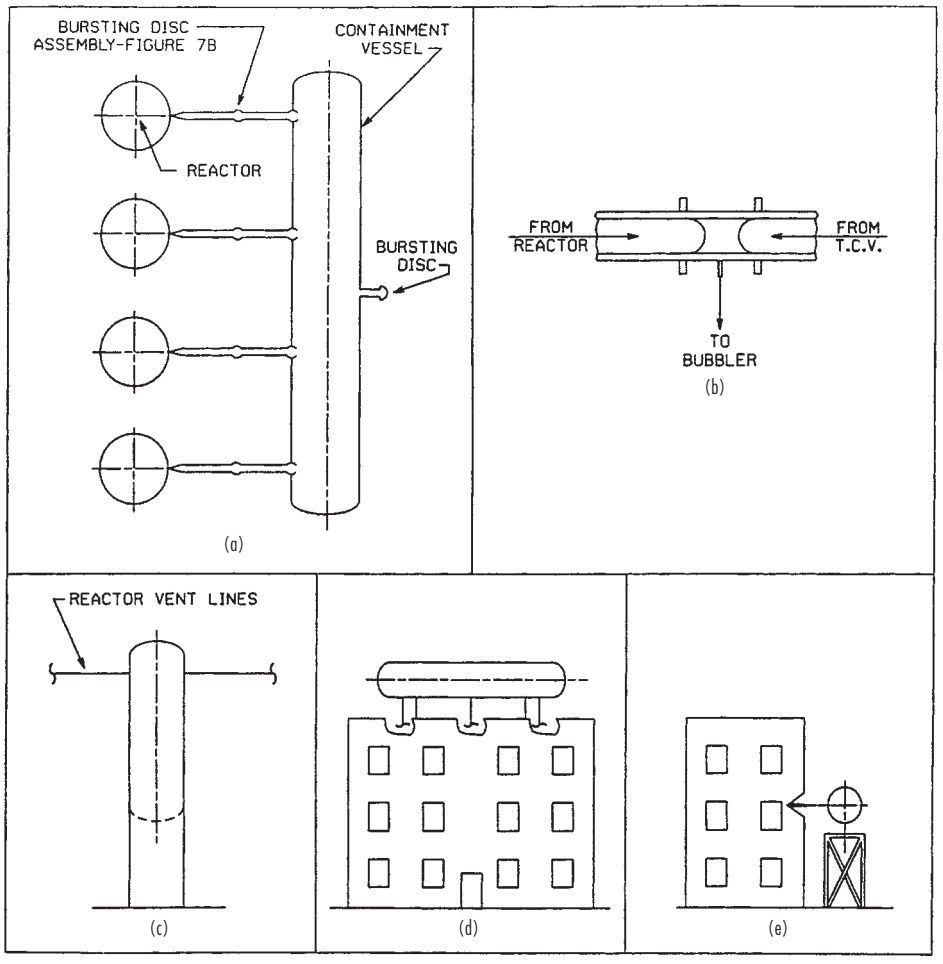


FIG. 26-22 Multireactor knockout (K-O) drum/catch tank: (*a*) plan view of reactors connected to horizontal containment vessel; (*b*) back-to-back bursting disc assembly; (*c*) elevation of self-supporting vessel; (*d*) elevation of horizontal vessel on roof of building; (*e*) elevation of horizontal vessel on side of building.

Performance Characteristics:

Quenching only saturated vapors with no inerts:

Cold quench liquid:

1. Sparging will condense the vapors effectively.
2. Sudden vapor condensation in the pool may cause water hammer if the holes are too big and the pressure drop is too low. Sonic hole velocity is desirable to avoid this problem.

Hot, nearly saturated quench liquid:

1. Sparging may not condense all the vapor. The injection of cold liquid spray in the vapor space should be considered.
2. Sudden vapor condensation in the pool is a minor problem.

Quenching only saturated vapors with some inerts:

1. Sparging may be ineffective in condensing all the condensable vapor.
2. A mass transfer device, such as a packed or trayed contact section, should be considered (see Fig. 26-21).

Quenching two-phase mixtures:

High volumetric vapor/liquid ratios ($r > 10$): where r = volumetric vapor flow rate/volumetric liquid flow rate.

1. The sparger design can be based on all vapor flow, but the heat balance must include the liquid.

Moderate volumetric vapor liquid ratios ($1 < r < 10$):

1. The liquid may inhibit the mass transfer rates needed to condense the vapors; sparging may, therefore, be less effective.
2. Sudden vapor condensation is of less concern.

Low volumetric vapor/liquid ratios ($r < 1$):

1. The mixture acts like a liquid and the vapor condensation is dependent on jet mixing. This will require a different type of sparger design.

Sizing and Design of Equipment The information in the following sections that pertain to the sizing and design of blowdown drums (catch tanks) and cyclone separators are for normal liquid-vapor systems (low-viscosity and nonfoamy or unstable foams). They are not applicable to high-viscosity (newtonian and non-newtonian) liquids and/or systems which exhibit surface-active foaming behavior, as no information is available at the present time as to the separation efficiency for these types of equipment. Quench tanks can usually handle high-viscosity liquids as well as stable foams.

Horizontal Blowdown Drum (See Fig. 26-16.) The two main criteria used in sizing horizontal blowdown drums or catch tanks are as follows.

1. The diameter must be sufficient to effect good vapor-liquid separation.
2. The total volume must be sufficient to hold the estimated amount of liquid carryover from the reactor. For a foamy discharge,

the holding volume should be greater than the reactor liquid volume (to be discussed further). One design method for sizing a horizontal blowdown drum is presented in API RP521 (1997). This may require a trial-and-error design procedure to arrive at an optimum drum size. Another procedure, which has been used in the industry by many companies, may be used to size horizontal blowdown drums more directly and is as follows:

1. Calculate the allowable vapor velocity U_a

$$U_a = k\sqrt{\frac{\rho_L - \rho_v}{\rho_v}} \tag{26-32}$$

where U_a = allowable vapor velocity, ft/s
ρ_L = liquid density, lb/ft^3
ρ_v = vapor density, lb/ft^3
k = capacity coefficient

Values of k reported in the technical literature have ranged from 0.157 to 0.40. A k value of 0.27 has resulted in conservatively sized blowdown drums, able to separate liquid droplets 300 μm in diameter and larger.

2. Calculate the vapor flow area A_v

$$A_v = \frac{Q_v}{U_a} \tag{26-33}$$

where A_v = vapor flow area, ft^2
Q_v = vapor flow rate, ft^3/s

3. Assume A_v occupies half of the drum area, so that the drum diameter is:

$$D_d = \sqrt{\frac{2A_v}{0.785}}, \text{ ft} \tag{26-34}$$

4. Determine the drum volume occupied by liquid V_L based on the following criteria:

a. For nonfoaming systems, V_L should be equal to the maximum working volume of the reactor.

b. For mildly foaming systems, which rapidly defoam, V_L should be a minimum of 1.5 times the maximum working volume of the reactor. Experimental data may indicate that V_L has to be even larger than this.

5. Ignoring both heads, calculate the drum length L:

$$L = \frac{2V_L}{0.785D_d^2} \tag{26-35}$$

where V_L = drum liquid volume, ft^3
L = drum length, ft

6. If the drum length is less than two to three times the diameter, the design is satisfactory. If L is greater than $3D_d$, assume a larger diameter and repeat the calculation until a satisfactory L/D_d ratio is achieved.

Another equation for quick sizing of horizontal knockout drums/catch tanks is presented by Tan (*Hydrocarbon Processing,* October 1967, p. 149). He recommends the following equation for calculating the drum diameter:

$$W = 360D^2\sqrt{(\rho_L - \rho_v)\frac{MP}{T}} \tag{26-36}$$

where W = vapor flow rate, lb/h
D = drum diameter, ft
ρ_L = liquid density, lb/ft^3
ρ_v = vapor density, lb/ft^3
M = molecular weight of vapor
P = pressure in the drum, psia
T = temperature of the vapor, °R

The author states that this equation is valid for the design of knockout drums which can separate liquid droplets of 400 μm and larger.

Cyclone Separator with Separate Catch Tank (See Figs. 26-17 and 26-18.) The sizing of a cyclone knockout drum for emergency relief systems is somewhat different from sizing a cyclone separator for normal process service for the following reasons:

1. In normal process service, the superficial vapor velocity at the inlet of tangential-entry vapor-liquid separators is limited to about 120 to 150 ft/s. Higher velocities may lead to:
   - Excessive pressure drop in the separator and in the inlet piping
   - Generation of fine mist in the inlet piping, which escapes collection in the separator
2. Inlet velocity restrictions do not apply in the design of separators for emergency relief systems because:
   - Pressure drop is usually not a penalty.
   - Escape of fine mist can usually be tolerated.

Sizing Procedure The cyclone is sized by choosing a superficial F-factor for the skirt in the range of 5.0 to 8.0. The higher value may be used for waterlike liquids; the lower value for liquids like molasses. If design F-factors exceed the range of 5 to 8, the liquid draining down the skirt is entrained and escapes with the vapor. These F-factors were determined in small-scale lab experiments using water and a high-polymer solution as the test liquids. The high-polymer solution had a viscosity that was molasses-like, probably in the range of 1500 cP. There were no liquids of intermediate viscosity used in the tests.

The F-factors of 5.0 and 8.0 are conservative in the opinion of the researcher who performed the experiments (private communication from E. I. du Pont de Nemours Co., Inc., to the DIERS Project).

The F-factor is defined as follows:

$$F = V_v\sqrt{\rho_v} \tag{26-37}$$

or

$$F = \frac{G_v}{\sqrt{\rho_v}} \tag{26-38}$$

where V_v = superficial velocity, ft/s
ρ_v = vapor density, lb/ft^3
G_v = superficial vapor mass flux, lb/s·ft^2

The design procedure is as follows:

1. Calculate G_v

$$G_v = F\sqrt{\rho_v}, \text{ lb/s·ft}^2 \tag{26-39}$$

2. Calculate the skirt flow area

$$A_S = \frac{W}{3600G_v}, \text{ ft}^2 \tag{26-40}$$

where W = vapor flow rate, lb/h

3. Calculate skirt diameter

$$D_S = \sqrt{\frac{A_S}{0.785}}, \text{ ft} \tag{26-41}$$

4. Calculate all the other separator dimensions from the relationships given in Fig. 26-18.

When the pressure relief device is set to open at greater than 15 psig (critical flow will result), it is normally not necessary to be concerned about the pressure drop in the separator. If the liquid is to be drained from the separator during the emergency blowdown, a vortex breaker and false bottom should be used (Fig. 26-18, view BB).

If the liquid contents of the vented vessel are to be retained in the separator for subsequent disposition, the holdup capacity may be increased by increasing the height of the vessel to increase the total volume by an amount equal to the vented liquid volume.

Cyclone Separator with Integral Catch Tank (See Fig. 26-19.) The diameter of the knockout drum is calculated by the criteria given in the preceding section and Fig. 26-18. Since the liquid is also to be retained in the vessel, extend the shell height below the normal bottom tangent line to increase the total volume by an amount equal to the volume of the liquid carried over.

Quench Tank (See Figs. 26-20 and 26-21.)

General In comparison with design information on blowdown drums and cyclone separators, there is very little information in the open technical literature on the design of quench tanks in the chemical industry. What is available deals with the design of quench tanks (also called *suppression pools*) for condensation of steam or steam-water mixtures from nuclear reactor safety valves. Information and criteria from quench tanks in the nuclear industry can be used for the design of quench tanks in the chemical industry. There have been sev-

eral articles in recent years which provide more data for chemical industry quench tank design (AIChE-CCPS, 1997). The following sections summarize some of this information.

Design Criteria Pertinent criteria for quench tank sizing and design are presented below:

OPERATING PRESSURE There are three modes of operation of a quench tank: atmospheric pressure operation, nonvented operation, and controlled venting operation. Atmospheric operation is usually feasible when the effluent being emitted has a bubble point well above the maximum ambient temperature. A very small quantity of vapor escapes with the air that is displaced as the tank fills with the emergency discharge (typically about 0.2 percent of the reactor contents). Depending on the toxic or flammable properties of the vapor, the vent from the quench tank can be routed to the atmosphere or must be sent to a scrubber or flare.

In nonvented operation, no material is vented to the atmosphere, and this design is used when complete containment of the discharge is required. It is also used when the discharge mixture bubble point is close to or below the maximum ambient temperature and the concentration of noncondensable gas in the feed stream is very low. The tank design pressure is relatively high since the initial air in the tank is compressed by the rising liquid level, adding to the vapor pressure. The designer must take into consideration that the quench tank backpressure must be limited so as not to adversely affect the reactor relief system.

In controlled venting operation, the quench tank pressure is maintained at a desired level by a pressure controller/control valve system or pressure relief valve. This mode of operation is used when the discharge mixture bubble point is close to or below the maximum ambient temperature, and it is desired to limit the maximum quench tank pressure.

QUENCH LIQUID SELECTION The choice of the appropriate quench liquid depends on a number of factors. Water is usually the first quench liquid to consider, since it is nontoxic, nonflammable, compatible with many effluent vapors, and has excellent thermal properties. If water is selected as the quench liquid, the tank should be located indoors, if possible, to avoid freezing problems. If the tank has to be located outdoors in a cold climate, the addition of antifreeze is preferable to heat-tracing the tank, since overheating the tank can occur from tracing, thus reducing its effectiveness.

If other quench liquids are required, the liquid should have as many of the following properties as possible: compatibility with the discharge effluent, low vapor pressure, high specific heat, low viscosity, low flammability, low freezing point, high thermal conductivity, immiscibility with the discharge effluent, low cost, and ready availability.

QUENCH LIQUID QUANTITY A good discussion of the factors determining the quantity of quench liquid required is presented by CCPS (AIChE-CCPS, 1995).

When water is used as the quench medium and the effluent stream is a hydrocarbon or organic, separate liquid phases are often formed. In this case, heat transfer is the predominating mechanism during the quench. To achieve effective heat transfer, there must be a sufficient difference between the quench liquid temperature and the bubble point of the incoming effluent stream. The minimum temperature difference occurs at the end of the discharge, when the quench pool temperature is highest. A rule of thumb, from industry practice, is to allow a 10 to 20°C (18 to 36°F) ΔT. For atmospheric tank operation, the final quench liquid temperature is then set 10 to 20°C (18 to 36°F) below the normal boiling point of the final quench pool mixture. For nonvented or controlled venting operation, the final boiling point is elevated, permitting a greater design temperature rise and the use of less quench liquid. Therefore, the quench pool final temperature must be set 10 to 20°C (18 to 36°F) lower than the saturated temperature of the discharge effluent at the design maximum quench tank pressure.

The minimum capacity of quench liquid can be estimated by a heat balance, knowing the final quench pool temperature. The following equation given by Fauske (*International Symposium on Multi-Phase Transport and Particulate Phenomena,* December 15–17, 1986) can be used to calculate the minimum amount of quench liquid:

$$M = \frac{m_o(T_R - T_a)C_R}{(T_a - T_o)C_q} \tag{26-42}$$

where m_o = mass of reactants
T_R = temperature of reactants at relief set pressure
T_a = allowable temperature following complete quench
T_o = initial temperature of the quench fluid
C_q = specific heat of the quench fluid
C_R = specific heat of the reactants
(consistent English or SI units)

The preceding equation assumes the reaction is completely quenched immediately after the relief point is reached. This behavior is closely approximated if the reaction stops in the quench pool and the reactor empties quickly and thoroughly. If the reaction continues in the quench pool, the temperature T_R should be increased to the maximum adiabatic exotherm temperature. An equation is presented by CCPS (AIChE-CCPS, 1997) that includes the heat of reaction. In some cases, an experiment is necessary to confirm that the reaction indeed stops in the quench pool.

It is good practice to provide 10 to 20 percent more quench liquid than the minimum amount calculated.

QUENCH TANK VOLUME The total volume of the quench tank should be equal to the sum of the following volumes:

Quench liquid required
Liquid entering in the multiphase effluent stream
Liquid condensed from vapors in entering the effluent stream
Freeboard for noncondensables (a minimum of 10 percent is recommended)

QUENCH TANK GEOMETRY Quench tanks can have any of the following three types of geometry:

- Horizontal cylindrical vessel
- Vertical cylindrical vessel
- Concrete pit (usually rectangular)

Usually, the geometry is determined by space limitations. Both horizontal or vertical cylindrical vessels are designed as pressure vessels, and for pressures up to 50 psig, an L/D ratio of 2 to 3 results in an economic design.

SPARGER DESIGN The effluent stream should be discharged into the quench liquid by means of a sparger, which breaks it up into small jets to provide good heat and mass transfer. The sparger design must also incorporate the following capabilities:

- Maximize momentum-induced recirculation in the quench pool
- Provide adequate flow area (cross section for pressure relief without imposing high backpressure)
- Minimize shock due to vapor bubble collapse
- Minimize unbalanced momentum forces

Figure 26-20 shows conventional quench tank sparger arrangements. As can be seen in this figure, the sparger can be of the following types:

- Vertical straight pipe sparger
- Tee sparger
- Four-armed cross sparger

The following design criteria are recommended:

1. For effluent streams consisting of only liquid and vapor, hole diameters ranging from ⅛ to ½ in are recommended. Larger hole diameters (up to 2 in) may be required if the blowdown stream contains solids (polymers and/or catalyst). However, the violently collapsing vapor bubbles create a water hammer effect which increases in severity with hole size.

2. Sonic hole velocity is desirable in smaller holes and is essential in ½- to 2-in holes. A minimum sparger pressure drop of 10 psi should be used.

3. The number of holes should provide at least 0.2 holes per square foot of pool cross-sectional area. The flow area of the manifold and/or distributor piping should be at least 2 times the total area of the sparger holes. This generally ensures that the pressure drop across the holes will be at least 10 times the pressure drop in the distributor.

4. To balance high-velocity momentum forces, a symmetrical sparger design must be used. This can be a vertical straight pipe, a tee-shaped, or a cross-shaped quencher arm configuration with rows of holes on opposite sides of the pipe, which helps to balance piping forces (see Fig. 26-20). This arrangement also enhances the momentum-induced recirculation of quench liquid and maximizes the temperature difference for heat transfer. A center-to-center hole spacing

of at least two to three hole diameters is recommended, which will minimize the coalescence of the discharging jets into larger, less effective jets.

The quencher arm should be anchored to prevent pipe whip. It should also extend to the length (for horizontal vessels) or the height (for vertical vessels) of the vessel to evenly distribute the vapors in the pool.

When quenching effluents discharged by safety valves, it is preferable to use a straight, vertical sparger with holes in the end cap as well as in the pipe side walls. This is recommended to minimize the possibility of liquid hammer, which can occur more readily in horizontal spargers. The liquid hammer usually occurs for the following reasons: as the relief valve opens for the first time, the pressure spike is cushioned by the air trapped in the vent line. This air is blown out. If the valve recloses, the line may cool, causing slugs of condensate to accumulate. When the valve reopens, the slugs will accelerate to very high velocities and impact any elbows and end caps of the sparger. In severe cases, the sparger-arm end caps can be knocked off. The preceding recommendation avoids turns and the holes in the end cap provide some relief from the pressure spike.

Mass-Transfer Contact Section Where there is a strong possibility that not all of the incoming vapors will be condensed in the pool, a direct-contact mass-transfer section is superimposed on the quench tank. This can be a baffle-tray section (as shown in Fig. 26-21) or a packed column section.

The design of direct-contact mass-transfer columns is discussed in detail by Scheiman (*Petro Chemical Engr.* **37**(3): 29–33, 1965; ibid. **37**(4): 75, 78–79) and Fair (*Chem. Eng.,* June 12, 1972).

Multireactor Knockout Drum/Catch Tank (See Fig. 26-22.)

Vessel Sizing The area needed for vapor disengaging is calculated by the equations given earlier in the section on horizontal blowdown drums.

The diameter and length (or height) are determined by considering a number of factors as follows:

1. The length should be sufficient to extend beyond the locations of the reactors discharging into the vessel so as to simplify discharge pipe runs (for a horizontal vessel).
2. The height should not greatly exceed the height of the building (for vertical vessels).
3. The diameter should be sufficient to allow attenuation of the shock wave leaving the deflector plate.
4. The diameter should be sufficient to allow installation of the pipes and deflector plates in such a way as not to interfere directly with one another (particularly important for vertical vessels).
5. The cost of pressure vessels increases as the diameter increases.
6. An upper limit to the diameter is set by the need to transport complete cylindrical sections from manufacturer to site.
7. The volume of liquid in the reactor or reactors (assuming more than one vents at the same time) must be determined.

Mechanical Design Considerations The paper by Speechly et al., ("Principles of Total Containment System Design," presented at *I. Chem. E. Northwestern Branch Meeting,* 1979) discusses a number of pertinent design features, as follows:

1. Each vent device discharge pipe is extended into the vessel and its end is fitted with a deflector device. This disperses the jet stream of solids (catalyst) and liquids discharged and dissipates this force, which should otherwise be exerted on the vessel wall immediately opposite.
2. The deflector device (baffle plate) must be carefully designed as described by Woods (*Proc. Inst. Mech. Engrs.* **180,** part 3J: 245–259, 1965–1966).
3. Isolate the catch tank from both reaction loads and forces generated by thermal expansion of the pipes; the pipes can be designed to enter the vessel through a sliding gland. Depending on layout, vessels which tend to have shorter, stiffer pipes between the building and the vessel may also require flexible bellows to be incorporated in the pipes.
4. There are usually several reactors linked to a single catch tank. To ensure that rupture of a disk on one reactor does not affect the others, each reactor is fitted with a double-rupture-disk assembly. The use of double rupture disks in this application requires installation of a leak detection device in the space between the two disks, which must also prevent a pressure buildup from occurring within this space. Otherwise, under some circumstances it is possible for a pinhole-type leakage in one disk to cause a pressure to be retained in the space between the two disks. In this event, the pressure at which the disks would rupture could be increased significantly. This condition could therefore render ineffective the protection of the reactor system itself.

For additional details on the design of blowdown drums, cyclone separators, and quench tanks, such as mechanical design, thrust forces, ancillary equipment, and safety considerations, refer to the books and articles listed in the General References.

FLAME ARRESTERS

General References: "Deflagration and Detonation Flame Arresters," *Guidelines for Engineering Design for Process Safety,* chap. 13, CCPS-AICE, 1993. Ibid., chap. 15, "Effluent Disposal Systems." Howard, W. B., "Flame Arresters and Flashback Preventers," *Plant/Operations Progress,* vol. 1, no. 4, 1982. Howard, "Precautions in Selection, Installation and Use of Flame Arresters," *Chem. Eng. Prog.,* April 1992. Piotrowski, "Specification of Flame Arresting Devices for Manifolded Low Pressure Storage Tanks," *Plant/Operations Progress,* vol. 10, no. 2, April 1991. Roussakis and Lapp, "A Comprehensive Test Method for In-Line Flame Arresters," *Plant/Operations Progress,* vol. 10, no. 2, April 1991. NFPA 497A, *Recommended Practice for Classification of Class I Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, 1997.

General Considerations Flame arresters are passive devices designed to prevent propagation of gas flames through pipelines. Typical applications are to prevent flames entering a system from outside (such as via a tank vent) or propagating within a system (such as from one tank to another). Flame arrestment is achieved by a permeable barrier, usually a metallic matrix containing narrow channels, which removes heat and free radicals from the flame fast enough to both quench it within the matrix and prevent reignition of the hot gas on the protected side of the arrester. These metallic matrices are known as *elements.* Some preliminary considerations for arrester selection and placement are:

1. Identify the at-risk equipment and the potential ignition sources in the piping system to determine where arresters should be placed and what general type (deflagration or detonation, unidirectional or bidirectional) are needed.
2. Determine the worst-case gas mixture combustion characteristics, system pressure, and permissible pressure drop across the arrester, to help select the most appropriate element design. Not only does element design impact pressure drop, but the rate of blockage due to particle impact, liquid condensation, and chemical reaction (such as monomer polymerization) can make some designs impractical even if in-service and out-of-service arresters are provided in parallel.
3. The possibility of a stationary flame residing on the arrester element surface should be evaluated, and so should the need for additional safeguards, should such an event occur (see "Endurance Burn" section).
4. Consider any material of construction limitations due to reactive or corrosive stream components.
5. Consider upset conditions that could exceed the test conditions at which the arrester was certified. These include the gas composition with regard to concentration of sensitive constituents such as ethylene or hydrogen, maximum system pressure during an emergency shutdown, and maximum temperature. Under certain upset conditions such as a high-pressure excursion, there may be no flame arrester available for the task.
6. Consider the type and location of the arrester with respect to ease of maintenance, particularly for large in-line arresters.

These questions address the type of arrester needed, the appropriate location, and the best design with respect to flow resistance, maintainability, and cost. It should be recognized that while flame arrester effectiveness is high, it is not 100 percent. To maximize effectiveness, attention should be given to proper selection, application, and maintenance of the device. In the case of marine vapor control systems in the United States, the testing and application of flame arresters is regulated by the U.S. Coast Guard. In other cases, recent testing protocols have been developed to address most adverse conditions

encountered. Some arresters, such as hydraulic arresters and in-line types used to stop decomposition flames, have specialized applications for which general design and testing information are scarce. Where flame arresters are impractical, alternative strategies such as fast-acting valves, vapor suppression, and flammable mixture control should be considered.

Combustion: Deflagrations and Detonations A deflagration is a combustion wave propagating at less than the speed of sound as measured in the unburned gas immediately ahead of the flame front. Flame speed relative to the unburned gas is typically 10–100 m/s, although, owing to expansion of hot gas behind the flame, several hundred meters per second may be achieved relative to the pipe wall. The combustion wave propagates via a process of heat transfer and species diffusion across the flame front, and there is no coupling in time nor space with the weak shock front generated ahead of it. Deflagrations typically generate maximum pressures in the range 8–12 times the initial pressure. The pressure peak coincides with the flame front, although a marked pressure rise preceeds it; thus, the unburned gas is compressed as the deflagration proceeds, depending on the flame speed and vent paths available. The precompression of gas ahead of the flame front (also known as "cascading" or "pressure piling") establishes the gas conditions in the arrester when the flame enters it and hence affects both the arrestment process and the maximum pressure generated in the arrester body. A severe deflagration arrestment test involves placing a restricting orifice behind the arrester, which increases the degree of precompression. This is known as "restricted-end" deflagration testing.

As the deflagration flame travels through piping, its speed increases due to flow-induced turbulence and compressive heating of the unburned gas ahead of the flame front. Turbulence is especially enhanced by flow obstructions such as valves, elbows, and tees. Once the flame speed has attained the order of 100 m/s, a deflagration-to-detonation transition (DDT) can occur, provided that the gas composition is within the detonatable limits, which lie inside the flammable limits. The travel distance for this to occur is referred to as the *run-up* distance for detonation. This distance varies with the gas mixture sensitivity and increases with pipe diameter. Tabulated run-up distances are generally for straight pipe runs, and DDT can occur for much smaller distances in pipe systems containing flow obstructions. At the instant of transition, a transient state of *overdriven detonation* is achieved and persists for a distance of a few pipe diameters. Overdriven detonations propagate at speeds greater than the speed of sound (as measured in the burned gas immediately behind the flame front), and side-on pressure ratios (at the pipe wall) in the range 50 to 100 have been measured. The peak pressure is variable, depending on the amount of precompression during deflagration. A severe test for detonation-type flame arresters is to arrange for the arrester to encounter a series of overdriven detonations.

After the abnormally high velocities and pressures associated with DDT have decayed, a state of stable detonation is attained. A detonation is a combustion-driven shock wave propagating at the speed of sound, as measured in the burned gas immediately behind the flame front. Since the speed of sound in this hot gas is much larger than in the unburned gas or the ambient air, and the flame front speed is augmented by the burned gas velocity, stable detonations propagate at supersonic velocities relative to an external fixed point. The wave is sustained by chemical energy released by shock compression and ignition of the unreacted gas. The flame front is coupled in space and time with the shock front, with no significant pressure rise ahead of the shock front. The high velocities and pressures associated with detonations require special element design to quench the high-velocity flames plus superior arrester construction to withstand the associated impulse loading. Since this entails narrower and/or longer element channels plus bracing of the element facing, both inherent pressure drop and the possibility of fouling of detonation arresters should be considered.

The problem of flame arrestment, either of deflagrations or detonations, depends on the properties of the gas mixture involved plus the initial temperature and pressure. Gas mixture combustion properties cannot be quantified for direct use in flame arrester selection and only general characteristics can be assigned. For this reason, flame arrester performance must be demonstrated by realistic testing. Such testing has demonstrated that arresters capable of stopping even overdriven detonations may fail under restricted-end deflagration test conditions. It is important to understand the significance of the test conditions addressed and their possible limitations.

Combustion: Gas Characteristics and Sensitivity Combustion thermodynamic calculations allow determination of peak deflagration and detonation pressures, plus stable detonation velocity. The peak pressure calculation may be used to determine combustion product venting requirements, although a conservative volume increase of 9:1 may be used for essentially closed systems. Other relevant gas characteristics are entirely experimental. The sensitivity to detonation depends on the detonatable range and fundamental burning velocity, although no specific correlations or measures of sensitivity exist based on fundamental properties. It is often considered that detonation sensitivity and the degree of difficulty in arresting flames increase with lower National Electrical Code (NEC) Groupings. Hence, Group A gases (acetylene) will be most sensitive and Group D gases (such as saturated hydrocarbons) will be least sensitive. This empirical method of characterizing gases is typically used in selecting deflagration arresters, where successful testing using one gas in an NEC electrical group is assumed to apply for other gases in that group. It is cautioned that, where the maximum experimental safe gaps (MESGs) of two gases within a single NEC group are significantly different, the assumption of equivalent sensitivity is dubious. Regulations applying to detonation arresters in vapor control systems under the authority of the U.S. Coast Guard (USCG) provide that MESGs be solely used to characterize gases, under the assumption that mixtures with smaller MESGs are more difficult to stop. See "Deflagration and Detonation Flame Arresters," (1993) for a discussion of MESG plus tabulated values.

Corrosion Consideration should be given to possible corrosion of both the element material and the arrester housing, since corrosion may weaken the structure, increase the pressure drop, and decrease the effectiveness of the element. While the housing might be designed to have a corrosion allowance, corrosion of the element must be avoided by proper material specification. Common materials of construction include aluminum, carbon steel, ductile iron, and 316 stainless steel housings and aluminum or 316 stainless steel elements. While special materials such as Hastelloy might be used for situations such as high HCl concentrations it may be more cost effective to use a hydraulic arrester in such applications.

Directionality To select an arrester for any service, the potential sources of ignition must be established in relation to the pipe system and the equipment to be protected. The pipe connecting an arrester with an identified ignition source is the *unprotected side* of the arrester. The pipe connecting the arrester with at-risk equipment is the *protected side.* If the arrester will encounter a flame arriving only from one direction, a *unidirectional* arrester can be used. If a flame may arrive from either direction, a *bidirectional* arrester is needed. The latter are either symmetrically constructed or are certified by testing. Back-to-back use of unidirectional arresters will not usually be cost effective unless testing reveals a specific advantage such as increased allowable operating pressure during restricted-end deflagration testing.

Endurance Burn Under certain conditions, a successfully arrested flame may stabilize on the unprotected side of an arrester element. Should this condition not be corrected, the flame will eventually penetrate the arrester as the channels become hot. An endurance burn time can be determined by testing, which specifies that the arrester has withstood a stabilized flame without penetration for a given period. The test should address either the actual or worst-case geometry, since heat transfer to the element will depend on whether the flame stabilizes on the top, bottom, or horizontal face. In general, the endurance burn time identified by test should not be regarded as an accurate measure of the time available to take remedial action, since test conditions will not necessarily approximate the worst possible practical case. Temperature sensors may be incorporated at the arrester to indicate a stabilized flame condition and either alarm or initiate appropriate action, such as valve closure.

Installation End-of-line arresters should be protected using appropriate weather hoods or cowls. In-line arresters (notably detonation arresters) must be designed to withstand the highest line pressure

that might be seen, including upset conditions. The design should be verified by hydrostatic and pneumatic pressure tests. The piping system should be designed with adequate supports and should allow routine access to the arrester for inspection and maintenance.

Maintenance It is important to provide for arrester maintenance, both by selection of the most suitable arrester type and judicious location. Inspection and maintenance should be performed on a regular basis, depending on experience with the particular arrester in the service involved. It should also be carried out after successful function of the arrester. Some in-line designs allow removal, inspection, and cleaning of the element without the need to expand the line. Unit designs featuring multiple elements in parallel can reduce downtime by extending the period between cleaning. For systems which cannot be shut down during maintenance, parallel arresters incorporating a three-way valve may be used. Detonation arrester elements are especially prone to damage during dismantling, cleaning, and reassembly. Maintenance must be carefully done, avoiding sharp objects that could disable the delicate channels in the element. Spare elements should be available to reduce downtime and provisions made for storing, transporting, and cleaning the elements without damage.

Monitoring The differential pressure across the arrester element can be monitored to determine the possible need for cleaning. The pressure taps must not create a flame path around the arrester. It can be important to provide temperature sensors, such as thermocouples, at the arrester to detect flame arrival and stabilization. Since arrester function may involve damage to the arrester, the event of successful function (flame arrival) may be used to initiate inspection of the element for damage. If the piping is such that flame stabilization on the element is a realistic concern, action must be taken immediately upon indication of such stabilization (see also "Endurance Burn"). Such action may involve valve closure to shut off gas flow.

Operating Temperature and Pressure Arresters are certified subject to maximum operating temperatures and absolute pressures normally seen at the arrester location. Arrester placement in relation to heat sources, such as incinerators, must be selected so that the allowable temperature is not exceeded, with due consideration for the detonation potential as run-up distance is increased.

If heat tracing is used to prevent condensation of liquids, the same temperature constraint applies. In the case of in-line arresters, there may be certain upset conditions that produce unusually large system pressures outside the stipulated operating range of the arrester. Since the maximum operating pressure for a detonation arrester may be in the range of 16 to 26 psia, depending on the gas sensitivity and arrester design, it may be impossible to find a suitable arrester to operate during such an upset. The situation may be exacerbated by pressure drop across the device, caused by high flow and/or fouling.

Pressure Drop Flow resistance depends on flame arrester channel arrangement and on a time-dependent fouling factor due to corrosion or accumulation of liquids, particles, or polymers, depending on the system involved. Monomer condensation is a difficult problem, since inhibitors will usually be removed during monomer evaporation and catalysis might occur over particulates trapped in the element. Pressure drop can be a critical factor in operability, and cleaning may represent a large hidden cost.

Fouling may be mitigated in a number of ways. First, the least-sensitive element design can be selected, and in the case of end-of-line arresters, weather hoods or cowls can be used to protect against water or ice accumulation. Second, a fouling factor (20 percent or greater) might be estimated and an element with a greater tested flow capacity selected to reduce the pressure drop. This should be further increased if liquid condensation might occur. It is important that certified flow curves for the arrester be used rather than calculated curves, since the latter can be highly optimistic. Condensation and polymerization may be mitigated by geometry (minimizing liquid accumulation in contact with the element) and provision for drainage. Alternatively, the arrester may be insulated and possibly heat traced. Drains should not provide flame paths around the arrester or leak in either direction when closed. If heat tracing is used, the temperature must be limited to the certified operating range of the arrester.

In addition to using an arrester element with greater flow capacity, it is common to use two arresters in parallel where frequent cleaning is required, with one arrester in standby. A three-way valve can be used to allow uninterrupted operation during changeover. Where elements have an intrinsically high pressure drop, such as sintered metal elements used in acetylene service, multiple parallel elements can be used.

Deflagration Arresters The two types of deflagration arrester normally considered are the *end-of-line arrester* (Figs. 26-23 and 26-24) and the *tank vent deflagration arrester.* Neither type of arrester is designed to stop detonations. If mounted sufficiently far from the atmospheric outlet of a piping system, which constitutes the unprotected side of the arrester, the flame can accelerate sufficiently to cause these arresters to fail. Failure can occur at high flame speeds even without a run-up to detonation.

If atmospheric tanks are equipped with flame arresters on the vents, fouling or blockage by extraneous material can inhibit gas flow to the degree that the tank can be damaged by underpressure. API standards allow the use of pressure-vacuum (P/V) valves without flame arresters for free venting tanks on the basis that the high vapor velocity in the narrow gap between pressure pallet (platter) and valve body will prevent flashback. However, it is important to ensure that the pallet is not missing or stuck open, since this will remove the protection. Absence of the pallet was a listed factor in the 1991 Coode Island fire (State Coroner Victoria, Case No. 2755/91, Inquest into Fire at Coode Island on August 21 and 22, 1991, Finding). Whether flame arresters are used, proper inspection and maintenance of these vent systems is required.

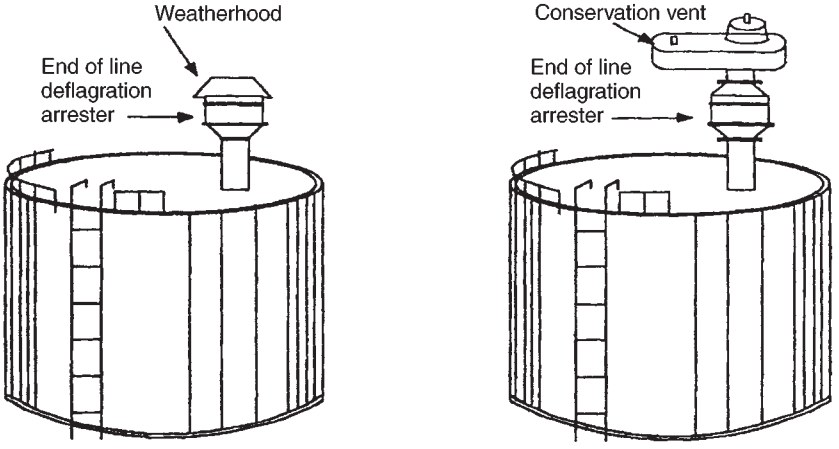


FIG. 26-23 Typical deflagration arrester installations.

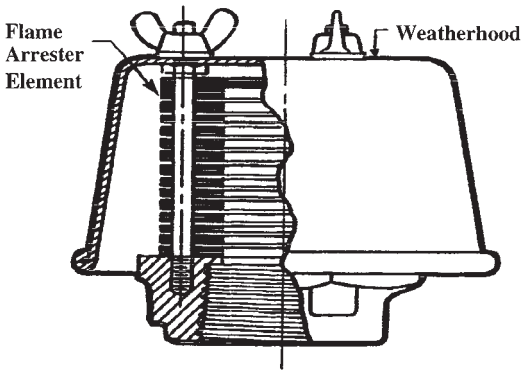


FIG. 26-24 Typical deflagration arrester design (end-of-line type).

End-of-line arresters are mounted at the outlet of a pipe system and go directly to the atmosphere, so there is no potential for significant flame acceleration in the pipe. Tank vent deflagration arresters are strictly limited by the approval agency, but for Group D gases they are typically mounted no more than 20 ft from the end of a straight pipe that vents directly to the atmosphere. The allowed distance must be established by proper testing with the appropriate gas mixture and the pipe diameter involved. Turbulence-promoting irregularities in the flow (bends, tees, elbows, valves, etc.) cannot be used unless testing has addressed the exact geometry. It is essential that run-up to detonation cannot occur in the available piping system, and run-up distance can be less than 2 ft for some fast-burning gases such as hydrogen in air (Group B). Thus the NEC Grouping of the gas mixture must be considered. More important, it must be emphasized that even if run-up to detonation does not occur, a deflagration arrester can fail if the flame speed is great enough. Thus the run-up distance is not an adequate criterion for acceptable location and this limitation can be determined only by realistic testing. A number of explosions have occurred due to misapplication of deflagration arresters where detonation arresters should have been used.

In certain exceptional cases, a specially designed deflagration arrester may be mounted in-line without regard to run-up distance. This can be done only where the system is known to be incapable of detonation. An example is the decomposition flames of ethylene, which are briefly discussed under "Special Arrester Types and Alternatives."

Detonation and Other In-Line Arresters If the point of ignition is remote from the arrester location, the arrester is an in-line type such as might be situated in a vapor collection system connecting several tanks (Fig. 26-25). Due to the possibility of DDT, most in-line arresters are designed to stop both deflagrations and detonations (including overdriven detonations) of the specified gas mixture. These are known as *detonation arresters.* Figure 26-26 shows a typical design. In some cases, in-line arresters need to stop deflagrations only. However, in such cases it must be demonstrated that detonations cannot occur in the actual pipework system; unless the gas mixture is intrinsically not capable of detonation, this requires full-scale testing using the exact pipe geometry to be used in practice, which must not be changed after installation.

Detonation arresters are typically used in conjunction with other measures to decrease the risk of flame propagation. For example, in vapor control systems, the vapor is often enriched, diluted, or inerted, with appropriate instrumentation and control (see "Effluent Disposal Systems," 1993). In cases where ignition sources are present or predictable (such as most vapor destruct systems), the detonation arrester is used as a last-resort method anticipating possible failure of vapor composition control. Where vent collection systems have several vapor/oxidant sources, stream compositions can be highly variable and

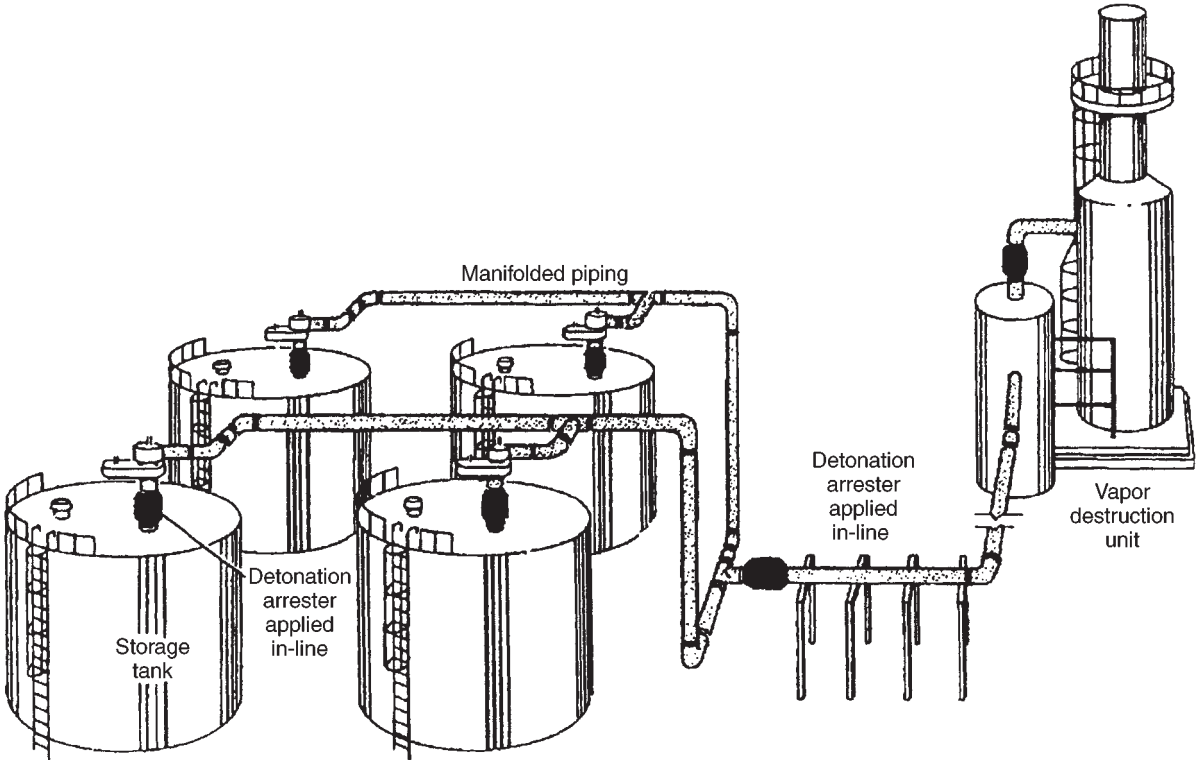


FIG. 26-25 Possible positions at which flame arresters may be placed (vapor control system).

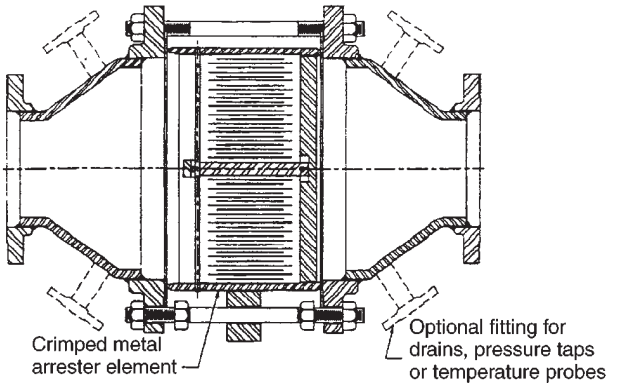


FIG. 26-26 Typical detonation arrester design (crimped-ribbon type).

this can be additionally complicated when upset conditions are considered. It is often cost effective to perform hazard analyses, such as fault tree analysis, to determine whether such vent streams can enter the flammable region and, if so, what composition corresponds to the worst credible case. Such an analysis is also suitable to assess alternatives to arresters.

Effect of Pipe Diameter Changes Arrester performance can be impaired by local changes in pipe diameter. It was shown that a minimum distance of 120 pipe diameters should be allowed between the arrester and any increase in pipe diameter, otherwise a marked reduction in maximum allowable operating pressure would occur. This impairment was observed during detonation testing but was most pronounced during restricted-end deflagration testing (Lapp and Vickers, *Int. Data Exchange Symp. on Flame Arresters and Arrestment Technology,* Banff, Alberta, October 1992). As a rule, arresters should be mounted in piping either equal to or smaller than the nominal size of the arrester.

Venting of Combustion Products As gas deflagrates or detonates in the piping system, there is a volume expansion of the products and an associated pressure increase. In some instances where the pipe system volume involved is relatively large, a significant overpressure might be developed in the vapor spaces of connected tanks, especially when vapor space is minimal due to high liquid level. It can be assumed that all the gas on the unprotected side of the arrester is converted to equilibrium products; the pressure is relieved via gas expansion into the entire system volume and to the atmosphere via any vent paths present. If heat losses are neglected by the assumption of high flame speeds or detonation and atmospheric venting paths are neglected, a conservative approach is that storage vessels be designed with a capacity to handle nine times the pipe volume on the unprotected side of the arrester. With regard to the high pressures associated with detonations, it has been shown (Lapp, *Independent Liquid Terminal Association Conference,* Houston, June 23, 1992) that detonation arresters attenuate the peak detonation pressure by up to 96 percent, depending on the arrester design, and therefore protect from much of the pressure pulse. To further reduce the pressure pulse, relief devices may be provided at the arrester.

Arrester Testing and Standards Regulatory and approval agencies and insurers impose acceptance testing requirements, sometimes as part of certification standards. The user may also request testing to demonstrate specific performance needs, just as the manufacturer can help develop standards. These interrelationships have resulted in several new and updated performance test procedures. *Listing* of an arrester by a testing laboratory refers only to performance under a defined set of test conditions. The flame arrester user should develop specific application requirements based on the service involved and the safety and risk criteria adopted.

A variety of test procedures and use guidelines have been developed. In addition, companies or associations may develop internal standards. The Federal Register, 33 CFR, Part 154, contains the USCG requirements for detonation arresters in marine vapor control systems. Other U.S. procedures are given in ASTM F 1273-91, UL 525, FM Procedure Classes 6061 and 7371, and API Publications 2028 and 2210. Outside the United States, procedures are given in Canada's CSA Standard Z 343, Rev. 12, 1993, the United Kingdom's British Standard BS 7244, Germany's DIN/CEN Draft Standard of the DAbF Subcommittee on Standardization, June 1991 (developed through the Federal Physical Technical Institute, PTB), and the International Maritime Organization (IMO) Standard MS/Circ. 373, Rev. 1, 1988. For U.S. mining applications, the Mine Safety and Health Administration (MSHA) provides regulation and guidance—for example, in CFR Title 30, Part 36.

Deflagration Arrester Testing For end-of-line and tank vent flame arresters, approval agencies may require manufacturers to provide users with data for flow capacity at operating pressures, proof of success during an endurance burn or continuous flame test, evidence of flashback test results (for end-of-line arresters) or explosion test results (for in-line or tank vent arrester applications), hydraulic pressure test results, and results of a corrosion test.

Endurance burn testing generally implies that the ignited gas mixture and flow rate be adjusted to give the worst-case heating (based on temperature observations on the protected side of the element surface), that the burn continue for a specified duration, and that flame penetration not occur. Continuous flame testing implies that a gas mixture and flow rate be established at specified conditions and burn on the flame arrester for a specified duration. The endurance burn test is usually a more severe test than the continuous burn. In both cases the flame arrester attachment configuration and any connecting piping or valves should be installed as in the plant design.

Flashback tests incorporate a flame arrester on top of a tank, with a large plastic bag surrounding the flame arrester. A specific gas mixture (for example, propane, ethylene, or hydrogen at the most sensitive composition in air) flows through and fills the tank and the bag. Deflagration flames initiated in the bag (three at different bag locations) must not pass through the flame arrester into the tank. On the unprotected side, piping and attachments such as valves are included as intended for installation; a series of tests—perhaps ten—is conducted.

Whatever the application, a user should be aware that not all test procedures are the same, are of the same severity, or use the same rating designations. Therefore, it is important to review the test procedure and determine whether the procedure used is applicable to the intended installation and potential hazard the flame arrester is meant to prevent.

Detonation Arrester Testing Requirements are described by various agencies in the aforementioned documents (UL 525, etc.). For installations governed by the USCG in Appendix A of 33 CFR, Part 154 (Marine Vapor Control Systems), the USCG test procedures must be followed. These are similar but not identical to those of other agencies listed (for a discussion of differences, see "Deflagration and Detonation Flame Arresters," 1993).

Detonation arresters are extensively tested for proof of performance against deflagrations, detonations, and endurance burns. In the United States, arrester manufacturers frequently test detonation arresters according to the USCG protocol; other test standards might alternatively or additionally be met. Under this protocol, the test gas must be selected to have either the same or a lower MESG than the gas in question (MESG means *maximum experimental safe gap*). Typical MESG benchmark gases are stoichiometric mixtures of propane, hexane, or gasoline in air to represent Group D gases having an MESG equal to or greater than 0.9 mm and ethylene in air to represent Group C gases with an MESG no less than 0.65 mm. Commercially available arresters are typically certified for use with one or another of these benchmark gas types. An ethylene-type arrester is selected should the gas in question have an MESG less than 0.9 mm but not less than 0.65 mm. Five low- and five high-overpressure deflagration tests are required with and without a flow restriction on the protected side. Of these 20 tests, the restricted-end condition is usually the more severe and often limits the maximum initial pressure at which the arrester will be suitable. Five detonation tests and five overdriven detonation tests are also required, which may involve additional run-up piping and turbulence promoters in order to achieve DDT at the arrester. If these tests are successful, an endurance burn test is required. This test does not use propane for

Group D gases, but hexane or gasoline, owing to their lower autoignition temperatures. For Group C tests, ethylene can be used for all test stages.

Shortcomings in the use of MESG to characterize gases, in the use of stoichiometric compositions for deflagration tests, and nonoptimization of test geometry have been recognized ("Deflagration and Detonation Flame Arresters," 1993). The user has the option to request additional tests to address such concerns and may wish to test actual stream compositions rather than simulate on the basis of MESG values.

Special Arrester Types and Alternatives Several types of *unlisted* arresters (water seals, packed beds, velocity-type devices, and fast-acting valves) mentioned in API 2028 are described more fully in Howard (1982). There are few design or test data for hydraulic and packed-bed arresters; some types are designed and used by individual companies for specific applications, while others are commercially available. Figure 26-27 shows some special arrester types.

Decomposition Flame Arresters Above certain minimum pipe diameters, temperatures, and pressures, some gases may propagate decomposition flames in the absence of oxidant. Special in-line arresters have been developed (Fig. 26-27). Both deflagration and detonation flames of acetylene have been arrested by hydraulic valve arresters, packed beds (which can be additionally water-wetted), and arrays of parallel sintered metal elements. Information on hydraulic and packed-bed arresters can be found in the Compressed Gas Association Pamphlet G1.3, "Acetylene Transmission for Chemical Synthesis." Special arresters have also been used for ethylene in 1000- to 1500-psi transmission lines and for ethylene oxide in process units. Since ethylene is not known to detonate in the absence of oxidant, these arresters were designed for in-line deflagration application.

Alternatives to Arresters Alternatives to the use of flame arresters include fast-acting isolation valves, vapor suppression systems, velocity-type devices in which gas velocity is designed to exceed flashback velocity, and control of the flammable mixture (NFPA 69 standard, "Explosion Prevention Systems"). The latter alternative frequently involves reduction of oxygen concentration to less than the limiting oxygen concentration (LOC) of the gas stream.

STORAGE AND HANDLING OF HAZARDOUS MATERIALS

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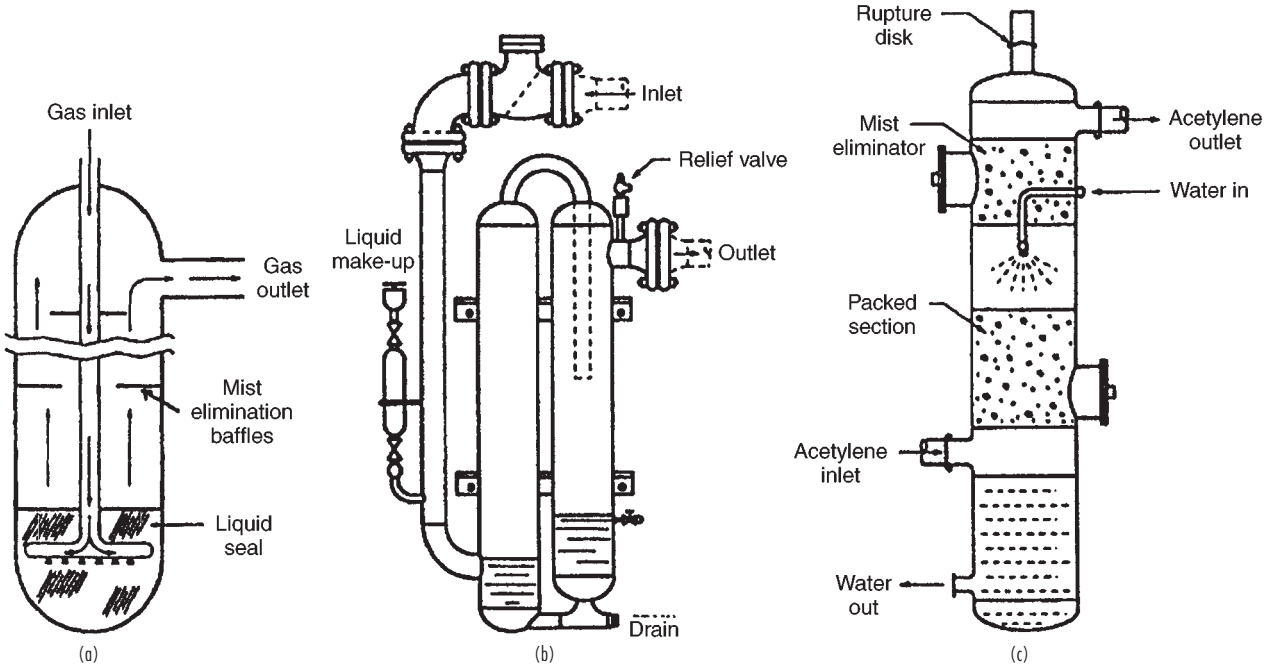


FIG. 26-27 Some special arrester designs: (*a*) liquid seal arrester; (*b*) Linde hydraulic seal arrester; (*c*) wetted packed-bed acetylene decomposition arrester. (*Howard, 1982.*)

Introduction The storage and handling of toxic materials involve risks that can be reduced to very low levels by good planning, design, and management practices. Facilities that handle toxic materials typically represent a variety of risks, ranging from small leaks, which require prompt attention, to large releases, which are extremely rare in well-managed facilities but which have the potential for widespread impact (Arthur D. Little, Inc., and LeVine, 1988, p. 5ff, by permission).

It is essential that good techniques be developed for identifying significant hazards and mitigating them where necessary. Hazards can be identified and evaluated using approaches discussed in the section on hazard and risk analysis.

Loss of containment due to mechanical failure or misoperation is a major cause of chemical process accidents. The design of storage systems should be based on minimizing the likelihood of loss of containment, with the accompanying release of hazardous materials, and on limiting the amount of the release. An effective emergency response program that can reduce the impacts of a release should be available.

Toxicity and Toxic Hazard There is a difference between toxicity and toxic hazard:

- Toxicity is the ability to cause biological injury.
- Toxicity is a property of all materials—even salt, sugar, and water.
- Toxicity is related to dose and degree of hazard associated with a material. Dose is time- and duration-dependent, in that dose is a function of exposure (concentration) times duration.

Toxic hazards may be caused by chemical means, radiation, and noise. Routes of exposure are: (1) eye contact, (2) inhalation, (3) ingestion, (4) skin contact, and (5) ears (noise). An *Industrial Hygiene Guide* (IHG) is based on exposures for an 8-h day, 40-h week, and is not to be used as a guide in the control of health hazards. It is not to be used as a fine line between safe and dangerous conditions.

A material that has a high toxicity does not necessarily present a severe toxic hazard. For example, a ton of lead arsenate spilled in a busy street is unlikely to poison members of the public just a short distance from the spill, because it is not mobile. It could be carefully recovered and removed and would present a low risk to the general public, even though it is extremely toxic. On the other hand, a ton of liquefied chlorine spilled on the same street could become about 11,000 ft^3 of pure gas. The IDLH for chlorine is 25 ppm. This is a concentration such that immediate action is required. Thus, the one ton of chlorine, if mixed uniformly with air, could create a cloud of considerable concern, having a volume of about 4.4×10^8 ft^3 or a sphere 770 ft in diameter. This could quickly spread over downwind areas and prove fatal to people near the spill site, causing toxic effects among hundreds of others in the downwind direction.

Measures of inhalation toxicity include ERPG, TLV, TLV-STEL, TLV-TWA, PEL, and IDLH.

- ERPG is defined in the section on hazard and risk analysis.
- TLV means *threshold limit value* (established by the American Conference of Government Industrial Hygienists, or ACGIH). TLV-C is the concentration in air that should not be exceeded during any part of the working exposure.
- TVL-STEL is a 15-min, time-weighted average concentration to which workers may be exposed up to four times per day with at least 60 min between successive exposures with no ill effect if the TLV-TWA is not exceeded (developed by the ACGIH).
- TLV-TWA is the time-weighted average concentration limit for a normal 8-h day and 40-h workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (developed by the ACGIH).
- PEL means *permissible exposure level* (similar to TLV but developed by the National Institute for Occupational Safety and Health, or NIOSH).
- IDLH means *immediately dangerous to life and health.* This is a concentration at which immediate action is required. The exact effect on an individual depends on the individual's physical condition and susceptibility to the toxic agent involved. It is the maximum airborne contamination concentration from which one could escape within 30 min without any escape-impairing symptoms or irreversible health effects (developed by NIOSH).

Storage

Storage Facilities The Flixborough disaster (Lees, 1980) occurred on June 1, 1974, and involved a large, unconfined vapor cloud explosion (or explosions—there may have been two) and fire that killed 28 people and injured 36 at the plant and many more in the surrounding area. The entire chemical plant was demolished and 1821 houses and 167 shops were damaged.

The results of the Flixborough investigation made it clear that the large inventory of flammable material in the process plant contributed to the scale of the disaster. It was concluded that "limitations of inventory should be taken as specific design objectives in major hazard installations." It should be noted, however, that reduction of inventory may require more frequent and smaller shipments and improved management.

There may be more chances for errors in connecting and reconnecting with small shipments. Quantitative risk analysis of storage facilities has revealed solutions that may run counter to intuition (Schaller, *Plant/Operations Progress,* **9**(1), 1990). For example, reducing inventories in tanks of hazardous materials does little to reduce risk in situations where most of the exposure arises from the number and extent of valves, nozzles, and lines connecting the tank. Removing tanks from service altogether, on the other hand, helps. A large pressure vessel may offer greater safety than several small pressure vessels of the same aggregate capacity because there are fewer associated nozzles and lines. Also, a large pressure vessel is inherently more robust, or it can economically be made more robust by deliberate overdesign than can a number of small vessels of the same design pressure. On the other hand, if the larger vessel has larger connecting lines, the relative risk may be greater if release rates through the larger lines increase the risk more than the inherently greater strength of the vessel reduces it. In transporting hazardous materials, maintaining tank car integrity in a derailment is often the most important line of defense in transportation of hazardous materials.

Safer Storage Conditions The hazards associated with storage facilities can often be reduced significantly by changing storage conditions. The primary objective is to reduce the driving force available to transport the hazardous material into the atmosphere in case of a leak (Hendershot, 1988). Some methods to accomplish this follow.

Dilution Dilution of a low-boiling hazardous material reduces the hazard in two ways:

1. The vapor pressure is reduced. This has a significant effect on the rate of release of material boiling at less than ambient temperature. It may be possible to store an aqueous solution at atmospheric pressure, such as aqueous ammonium hydroxide instead of anhydrous ammonia.
2. In the event of a spill, the atmospheric concentration of the hazardous material will be reduced, resulting in a smaller hazard downwind of the spill.

The reduction of vapor pressure by diluting ammonia, monomethylamine, and hydrochloric acid with water is shown in Table 26-9.

TABLE 26-9 Vapor Pressure of Aqueous Ammonia, Hydrochloric Acid, and Monomethylamine Solutions

Ammonia at 21°C		Monomethylamine at 20°C		Hydrochloric acid at 25°C	
Concentration wt.%	Vapor pressure, atm	Concentration wt.%	Vapor pressure, atm	Concentration wt.%	Vapor pressure, atm
100 (anhydrous)	8.8	100 (anhydrous)	2.8	100 (anhydrous)	46.1
48.6	3.0	50	0.62	41	1.0
33.7	1.1	40	0.37	38	0.36
28.8	0.75			32	0.055

SOURCE: Hendershot, 1988, by permission.

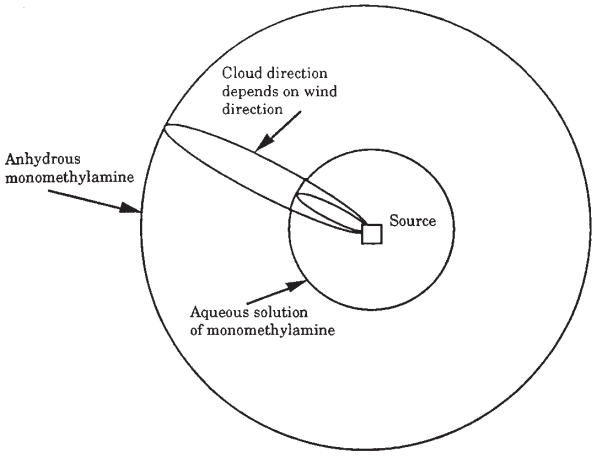


FIG. 26-28 Relative hazard zones for anhydrous and aqueous monomethylamine releases—relative distance within which there is a specified atmospheric concentration of monomethylamine and aqueous monomethylamine. (*Hendershot, 1988, by permission.*)

The relative size of hazard zones from possible loss of containment and releases to the atmosphere is much smaller for the cases in which the material is diluted, compared to the anhydrous materials. This is illustrated in Fig. 26-28 for monomethylamine.

The larger circle is the area that could be exposed to a specified atmospheric concentration of monomethylamine stored as an anhydrous liquid. The smaller circle is the area that could be exposed to a specified atmospheric concentration of monomethylamine stored as an aqueous solution. The elliptical figures represent a gas cloud caused by an east-southeast wind.

Refrigeration Loss of containment of a liquefied gas under pressure and at atmospheric temperature causes immediate flashing of a large proportion of the gas. This is followed by slower evaporation of the residue. The hazard from a gas under pressure is normally much less in terms of the amount of material stored, but the physical energy released if a confined explosion occurs at high pressure is large.

Refrigerated storage of hazardous materials that are stored at or below their atmospheric boiling points mitigates the consequences of containment loss in three ways:

1. The rate of release, in the event of loss of containment, will be reduced because of the lower vapor pressure in the event of a leak.
2. Material stored at a reduced temperature has little or no superheat and there will be little flash in case of a leak. Vaporization will be mainly determined by liquid evaporation from the surface of the spilled liquid, which depends on weather conditions.
3. The amount of material released to the atmosphere will be further reduced because liquid entrainment from the two-phase flashing jet resulting from a leak will be reduced or eliminated.

Refrigerated storage is most effective in mitigating storage facility risk if the material is refrigerated when received. Much of the benefit of refrigerated storage will be lost if the material is received at ambient temperature under its vapor pressure in a transport container. The quantity of material that could be released during unloading may be larger because unloading lines are normally sized to rapidly unload a truck or rail car and are often larger than the process feed lines. Thus, if the material is shipped at ambient temperature, the benefits of refrigeration will not be available during the operations with the highest release potential.

The economics of storage of liquefied gases are such that it is usually attractive to use pressure storage for small quantities, pressure or semirefrigerated storage for medium to large quantities, and fully refrigerated storage for very large quantities. Quantitative guidelines are available from Lees (1980, pp. 271–272).

It is generally considered that there is a greater hazard in storing large quantities of liquefied gas under pressure than at low temperatures and low pressures. The trend is toward replacing pressure storage by refrigerated low-pressure storage for large inventories. However, it is necessary to consider the risk of the entire system, including the refrigeration system, and not just the storage vessel. The consequences of failure of the refrigeration system must be considered. Each case should be carefully evaluated on its own merits. In most cases, refrigerated storage of hazardous materials is undoubtedly safer, such as in the storage of large quantities of liquefied chlorine.

Design of Liquid Storage So Leaks and Spills Do Not Accumulate Under Tanks or Equipment Around storage and process equipment, it is a good idea to design dikes that will not allow toxic and flammable materials to accumulate around the bottom of tanks or equipment in case of a spill. If liquid is spilled and ignites inside a dike where there are storage tanks or process equipment, the fire may be continuously supplied with fuel and the consequences can be severe. It is usually much better to direct possible spills and leaks to an area away from the tank or equipment and provide a fire wall to shield the equipment from most of the flames if a fire occurs. The discussion on BLEVEs later in this section shows a design for diking for directing leaks and spills to an area away from tanks and equipment.

The surface area of a spill should be minimized for materials that are highly toxic and have a significant vapor pressure at ambient conditions, such as acrylonitrile or chlorine. This will make it easier and more practical to collect vapor from a spill or to suppress vapor release with foam. This may require a deeper nondrained dike area than normal or some other design that will minimize surface area, in order to contain the required volume. It is usually not desirable to cover a diked area to restrict loss of vapor if the spill consists of a flammable or combustible material.

Minimal Use of Underground Tanks The U.S. Environmental Protection Agency's (USEPA) Office of Underground Storage Tanks defines underground tanks as those with 10 percent of more of their volume, including piping, underground. An aboveground tank that does not have more than 10 percent of its volume (including piping) underground is excluded from the underground tank regulations. Note, however, that a 5000-gal tank sitting wholly atop the ground but having 1400 ft of 3-in buried pipe or 350 ft of 6-in buried pipe is considered an underground storage tank.

At one time, burying tanks was recommended because it minimized the need for a fire protection system, dikes, and distance separation. At many companies this is no longer considered good practice. Mounding, or burying tanks above grade, has most of the same problems as burying tanks below ground and is usually not recommended.

Problems with buried tanks include:

- Difficulty in monitoring interior and exterior corrosion (shell thickness)
- Difficulty in detecting leaks
- Difficulty of repairing a tank if the surrounding earth is saturated with chemicals from a leak
- Potential contamination of groundwater due to leakage

Governmental regulations concerning buried tanks are becoming stricter. This is because of the large number of leaking tanks that have been identified as causing adverse environmental and human health problems.

Consequences of Leaking Underground Tanks The following is a real possibility (Russell and Hart, 1987). A site where an underground tank has been used is found to have leaked. If the leak is not cleaned up to "background" levels by the time an environmental regulatory agency is involved, the agency may decide that a portion of the plant must be designated as a waste disposal site. The plant could then be required to provide a waste site closure plan, hold public hearings, place deed restrictions on the plant property, and, finally, provide a bond that would cover the cost of closing the site and also analyzing and sampling groundwater for up to 30 years.

Product leaking from an underground storage tank will migrate downward until it encounters the water table, where it will then flow with the groundwater, leaving a long trail of contaminated soil. Above the water table, some product will be absorbed on the soil particles and in the pore space between the soil particles. If the soil is later saturated by water, product stored in the pore spaces may be released, causing a reappearance of the free product and movement of the material into previously unaffected soil.

The scope of the problem was revealed by the USEPA in 1983

when it reported that, in the United States, 11 million gallons of gasoline seep into the soil each year. Just one gallon of gasoline can make one million gallons of water unsafe to drink; one ounce would pollute an Olympic-size swimming pool full of drinking water. Most of the contaminated sites the USEPA has documented involve corroded single-wall steel tanks and piping that have been in the ground for at least 16 years (Semonelli, "Secondary Containment of Underground Storage Tanks," *Chem. Eng. Prog.,* June 1990). A number of states have enacted laws setting standards for underground storage tanks. The USEPA has issued regulations requiring notification to the appropriate regulatory agency about age, condition, and size for underground storage tanks containing commercial chemical products.

Secondary Containment for Underground Storage Acceptable secondary containment systems for underground storage are described as barriers either integral to the tank system design (such as double-walled tanks or double-walled pipes) or located within the underground storage tank system that present a barrier between all parts of the underground storage tank system and the environment. Double-walled tanks and piping should be considered for aboveground tanks and piping containing highly toxic liquids.

Concrete and fiberglass vaults are often used, although they can be subject to environmentally induced cracks. Soil and clay liners are not allowed. Flexible liner systems have been developed that may be a cost-effective and environmentally sound alternative. State-of-the-art liner technology has overcome many of the previous problems with seams, low mechanical strength, and chemical resistance.

Piping Systems for Underground Service An important consideration is the USEPA's concern over piping systems. For all underground storage tank systems, performance standards consistent with those for tanks were set for pipes and pipe systems. There is evidence that 84 percent of underground storage tank system test failures are due to loose tank fittings or faulty piping. Piping releases occur twice as often as tank releases. In particular, loose joints tend to occur. For hazardous substance underground storage tank systems, there are two options: trench liners and double-walled pipes. Double-walled pipes are difficult to assemble and are subject to failure caused by service conditions, such as frost heaves or pressure from above. Flexible trench liners (discussed previously) are becoming a popular solution to secondary containment of piping systems.

Detecting Leaks Small leaks are difficult to detect. The USEPA and American Petroleum Institute standard for nonleaking underground tanks is 0.05 gal/h (3.15 cm^3/min), above which a tank is considered to be leaking. Leak detection measurements can be influenced by many factors, making it difficult to detect small leaks.

Corrosion Problems Tanks subject to internal corrosion are not good choices for underground service because of the necessity of monitoring wall thickness. Underground tanks and piping of carbon steel should be considered for corrosion protection measures such as external tarlike coatings and magnesium anodes. Joints in underground piping should be minimized by welding. Pipes may use a combination of wrapping and sprayed-on coatings. When flanges are necessary, such as with valves, external coatings should be used.

Summary of Use of Underground Tanks Because of more stringent regulatory requirements, potential future liabilities, and the cost of building and operating underground storage tank systems, it may be inherently safer to use aboveground storage with suitable spacing, diking, and fire protection facilities. With modern technology, if it is necessary, it is possible to design underground storage systems with a high degree of integrity and which will make leaks to the environment highly unlikely, but the cost may be high.

Design of Tanks, Piping, and Pumps Six basic tank designs are used for the storage of organic liquids: (1) fixed roof, (2) external floating roof, (3) internal floating roof, (4) variable vapor space, (5) low-pressure tanks, and (6) high-pressure tanks. The first four tank designs listed are not generally considered suitable for highly toxic hazardous materials.

Low-Pressure Tanks (below 15 psig) Low-pressure storage tanks for highly hazardous toxic materials should meet, as a minimum, the American Petroleum Institute (API) 620 Standard, "Recommended Rules for the Design and Construction of Large Welded, Low-Pressure Storage Tanks" (*API Standards*). This standard covers tanks designed for all pressures under 15 psig. There are no specific requirements in API 620 for highly hazardous toxic materials.

API 650, "Welded Steel Tanks for Oil Storage" (*API Standards*) has limited applicability to storage of highly hazardous toxic materials because it prohibits refrigerated service and limits pressures to 2.5 psig and only if designed for certain conditions. Most API 650 tanks have a working pressure approaching atmospheric pressure and hence their pressure-relieving devices must vent directly to the atmosphere. Its safety factors and welding controls are less stringent than required by API 620. Another reference for the design of low-pressure storage tanks may be found in ANSI/API-620-1986.

Horizontal and vertical cylindrical tanks are used to store highly toxic liquids at atmospheric pressure. Horizontal, vertical, and spherical tanks are used for refrigerated liquefied gases that are stored at atmospheric pressure. The design pressure of tanks for atmospheric and low-pressure storage at ambient temperature should not be less than 100 percent of the vapor pressure of the material at the maximum design temperature. The maximum design metal temperature to be used takes into consideration the maximum temperature of material entering the tank and the maximum ambient temperature, including solar radiation effects.

Since discharges of vapors from highly hazardous toxic materials cannot simply be released to the atmosphere, the use of a weak seam roof is not normally acceptable. It is best that tanks be designed and stamped for 15 psig to provide maximum safety, and pressure relief systems must be provided to vent to equipment that can collect, contain, and treat the effluent.

The minimum design temperature should be the lowest temperature to which the tank will be subjected, taking into consideration the minimum temperature of material entering the tank, the minimum temperature to which the material may be autorefrigerated by rapid evaporation of low-boiling liquids or mechanically refrigerated, and the minimum ambient temperature of the area where the tank is located. API 620 provides for installations in areas where the lowest recorded one-day mean temperature is –50°F.

While either rupture disks or relief valves are allowed on storage tanks by Code, rupture disks by themselves should not be used on tanks for the storage of highly hazardous toxic materials since they do not close after opening and may lead to continuing release of toxic material to the atmosphere.

The API 620 Code requires a combined pneumatic hydrotest at 125 percent of design tank loading. In tanks designed for low-density liquid, the upper portion is not fully tested. For highly hazardous toxic materials, consideration should be given for hydrotesting at the maximum specified design liquid level. It may be required that the lower shell thickness be increased to withstand a full head of water and that the foundation be designed such that it can support a tank full of water or the density of the liquid if it is greater than water. Testing in this manner not only tests the containment capability of the tank, but it also provides an overload test for the tank and the foundation similar to the overload test for pressure vessels. API 620 also requires radiography.

Proper preparation of the subgrade and grade is extremely important for tanks that are to rest directly on grade. Precautions should be taken to prevent ground freezing under refrigerated tanks, as this can cause the ground to heave and damage the foundation or the tank. Designing for free air circulation under the tank is a method for passive protection from ground freezing.

Steels lose their ductility at low temperatures and can become subject to brittle failure. There are specific requirements for metals to be used for refrigerated storage tanks in API 620, Appendices Q and R.

Corrosive chemicals and external exposure can cause tank failure. Materials of construction should be chosen so that they are compatible with the chemicals and exposure involved. Welding reduces the corrosion resistance of many alloys, leading to localized attack at the heat-affected zones. This may be prevented by the use of the proper alloys and weld materials, in some cases combined with annealing heat treatment.

External corrosion can occur under insulation, especially if the weather barrier is not maintained or if the tank is operating at conditions at which condensation is likely. This form of attack is hidden and may be unnoticed for a long time. Inspection holes and plugs should

be installed in the insulation to monitor possible corrosion under the insulation.

High-Pressure Tanks (above 15 psig) The design of vessels above 15 psig falls within the scope of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, Section VIII "Pressure Vessels, Division I" and should be designated as lethal service if required. *Lethal service* means containing substances which are "poisonous gases or liquids of such a nature that a very small amount of the gas or vapor of the liquid mixed or unmixed with air is dangerous to life when inhaled. This class includes substances which are stored under pressure or may generate a pressure if stored in a closed vessel." This is similar to, but not exactly like, the same definition as that for "Category M" fluid service of the ASME Pressure Piping Code (see below). Pressure vessels for the storage of highly hazardous toxic materials should be designed in accordance with requirements of the ASME code even if they could be exempted because of high pressure or size. The code requires that the corrosion allowance be adequate to compensate for the more or less uniform corrosion expected to take place during the life of the vessel and not weaken the vessel below design strength.

Venting and Drainage In the installation of a storage tank, good engineering should go into the design of a drain and a vent. Low-pressure storage tanks are particularly susceptible to damage if good venting practices are not followed. A vent that does not function properly at all times may cause damage to the tank from pressure that is too high or too low. Vapors should go to a collection system, if necessary, to contain toxic and hazardous vents.

Piping Piping falls within Chapter VIII of the ASME Pressure Piping Code, "Piping for Category M Fluid Service." Category M Fluid Service is defined as "fluid service in which the potential for personnel exposure is judged to be significant and in which a single exposure to a small quantity of a toxic fluid, caused by leakage, can produce serious irreversible harm to persons on breathing or bodily contact, even when prompt restorative measures are taken."

Piping systems should meet the requirements for both Category M Fluid Service and for "severe cyclic conditions." Piping systems should be subjected to a flexibility analysis and, if found to be too rigid, flexibility should be added. Severe vibration pulsations should be eliminated. Expansion bellows, flexible connections, and glass equipment should be avoided. Pipelines should be designed with the minimum number of joints, fittings, and valves. Joints should be flanged or butt-welded. Threaded joints should not be used.

Instrumentation (Arthur D. Little, Inc., and Levine, 1986.) Instrument systems are an essential part of the safe design and operation of systems for storing and handling highly toxic hazardous materials. They are key elements of systems to eliminate the threat of conditions that could result in loss of containment. They are also used for early detection of releases so that mitigating action can be taken before these releases result in serious effects on people in the plant or in the public sector, or on the environment.

The basic approach is to direct the system to the safest operating level relative to people or the environment when any emergency condition is detected, including power loss. An important concept of process control safety is to have adequate redundancy to reduce unwanted shutdowns and maintain an adequate level of certainty that a safe state will result if a real emergency does occur. As far as possible, instruments should be of the fail-safe type.

Every effort should be made to eliminate direct (Bourdon-type) pressure gauges. Diaphragm pressure gauges constructed of appropriate corrosion-resistant materials are preferred. Flow limiters should be used to limit flow in case of loss of integrity.

An accurate indication of level is critical to the avoidance of overflow and other serious conditions in storage vessels. Level control is important to avoid overfilling to prevent a liquid release. A very low level can result in loss of pump suction and possible pump failure. Capacitance level sensors are often used because they require little maintenance and are highly reliable; since they give only point measurements, they are best used as backup for analogue devices such as differential pressure level gauges or strain gauges. Strain gauges (*load cells*) should be considered, as they are capable of high accuracy and do not require penetration of the containment vessel.

Flow measurements using nonintrusive or low mechanical action principles are desired, such as magnetic, vortex-shedding, or Coriolis-type flowmeters. Orifice plates are easy to use and reliable but have a limited range and may not be suitable for streams which are not totally clean. Rotameters with glass tubes should not be used.

Temperature measurements usually require intrusion into the fluid. Where thermowells are exposed to hazardous materials, they should comply with the same material requirements for vessels and pipes to reduce failure from erosion and corrosion. In storage tanks, tank temperature is often monitored but usually not controlled. Temperature indication is desirable to indicate that the tank contents are approaching a hazardous region and to indicate thermal stratification. For some materials, such as acrylic acid, temperature control is necessary during storage to prevent freezing if it gets too cold and prevent chemical reaction if it gets too warm.

Alarms should act as early warning devices to anticipate a potentially hazardous situation. Alarms that are essential to safety should be identified and classified separately from process alarms. Redundancy may be required.

Pumps and Gaskets Fugitive emissions often occur as a result of leakage of process materials through leak paths in rotating seals and susceptible gasketed joints such as are found in pipe flanges. When properly maintained, fugitive emissions from most conventional joints and sealing systems used in industry can be kept to a minimum. For volatile organic compounds (VOCs) this is usually significantly less than 500 ppm as measured at the leak path by a portable VOC analyzer specified in USEPA reference method 21 (40 CFR 60, Appendix A, Method 21). However, for some sealing systems such as packing glands on pump shafts in some services, the necessary maintenance frequency and potential risks of noncompliance have caused some companies to eliminate them from services where fugitive emissions are a concern and use tighter sealing systems such as mechanical seals instead. In services where entrained solids or fouling are not present to a significant extent and additional cost is justified, magnetic drive and canned-motor pumps, which have become more reliable and available in a wide variety of configurations and materials, are being used to virtually eliminate fugitive emissions from pumps. In services where fugitive emissions are a concern, valves such as quarter turn, diaphragm seal, or bellows seal valves, which are less susceptible to leakage, are sometimes being used in place of gate or globe valves with packed stem seals. However, under many service conditions, high-cost equipment options are not necessary to comply with the provisions of fugitive emission regulations. Properly maintained packing glands or single mechanical seals on valves and pumps can often meet all emissions requirements. An informed choice should be made when specifying new valves and pumps, considering factors such as the type of service, accessibility for maintenance, cost, and the degree of emission reductions which may be achieved.

The most common maintenance problem with centrifugal pumps is with the seals. Mechanical seal problems account for most of the pump repairs in a chemical plant, with bearing failures a distant second. The absence of an external motor (on canned pumps) and a seal is appealing to those experienced with mechanical seal pumps.

Sealless pumps are very popular and are widely used in the chemical industry. Sealless pumps are manufactured in two basic types: canned-motor and magnetic-drive. Magnetic-drive pumps have thicker "cans," which hold in the process fluid, and the clearances between the internal rotor and can are greater compared to canned-motor pumps. This permits more bearing wear before the rotor starts wearing through the can. Many magnetic-drive pump designs now have incorporated a safety clearance, which uses a rub ring or a wear ring to support the rotating member in the event of excessive bearing wear or failure. This design feature prevents the rotating member (outer magnet holder or internal rotating shaft assembly) from accidentally rupturing the can, as well as providing a temporary bearing surface until the problem bearings can be replaced. Because most magnetic-drive pumps use permanent magnets for both the internal and external rotors, there is less heat to the pumped fluid than with canned-motor pumps. Some canned-motor pumps have fully pressure-rated outer shells, which enclose the canned motor; others don't. With magnetic-drive pumps, containment of leakage through the can to the outer shell can be a

problem. Even though the shell may be thick and capable of holding high pressures, there is often an elastomeric lip seal on the outer magnetic rotor shaft with little pressure containment capability.

Canned-motor pumps typically have a clearance between the rotor and the containment shell or can, which separates the fluid from the stator, of only 0.008 to 0.010 in (0.20 to 0.25 mm). The can has to be thin to allow magnetic flux to flow to the rotor. It is typically 0.010 to 0.015 in (0.25 to 0.38 mm) thick and made of Hastelloy. The rotor can wear through the can very rapidly if the rotor bearing wears enough to cause the rotor to move slightly and begin to rub against the can. The can may rupture, causing uncontrollable loss of the fluid being pumped.

It should not be assumed that just because there is no seal, sealless pumps are always safer than pumps with seals, even with the advanced technology now available in sealless pumps. Use sealless pumps with considerable caution when handling hazardous or flammable liquids.

Sealless pumps rely on the process fluid to lubricate the bearings. If the wear rate of the bearings in the fluid being handled is not known, the bearings can wear unexpectedly, causing rupture of the can.

Running a sealless pump dry can cause complete failure. If there is cavitation in the pump, hydraulic balancing in the pump no longer functions and excessive wear can occur, leading to failure of the can. *The most common problem with sealless pumps is bearing failure, which occurs either by flashing the fluid in the magnet area because of a drop in flow below minimum flow or by flashing in the impeller eye as it leaves the magnet area.* It is estimated that nine out of ten conventional canned-motor pump failures are the result of dry running. Canned pumps are available which, their manufacturer claims, can be operated dry for as long as 48 h.

It is especially important to avoid deadheading a sealless pump. Deadheaded sealless pumps can cause overheating. The bearings may be damaged and the pump may be overpressured. The pump and piping systems should be designed to avoid dead spots when pumping monomers. Monomers in dead spots may polymerize and plug the pump. There are minimum flow requirements for sealless pumps. It is recommended that a recirculation system be used to provide internal pump flow whenever the pump operates. Inlet line filters are recommended, but care must be taken not to cause excessive pressure drop on the suction side. Typical inlet filters use sieve openings of 0.0059 in (0.149 mm).

For many plants handling monomers and other hazardous materials, sealless pumps are the first choice. They can practically eliminate the pump problems that can occur due to seal leaks, which can include product loss, flammability, waste disposal, and exposure of personnel to hazardous vapors.

A number of liquids require special attention when applying canned-motor and magnetic-drive pumps. For example, a low-boiling liquid may flash and vapor-bind the pump. Solids in the liquid can also be bad for a sealless pump. Low-viscosity (in the range of 1 to 5 cP [1×10^{-3} to 5×10^{-3} Ns/m^2]) fluids are normally poor lubricators and one should be concerned about selecting the right bearings. For viscosities less than 1 cP, it is even more important to choose the right bearing material.

The Dow Chemical Company recommends canned-motor pumps or magnetic-drive pumps for phosgene service. Phosgene is an example of an extremely hazardous material. These pumps should have a secondary containment such that failure of the can does not create a phosgene release. The secondary containment should meet pipe specifications for pressure or relieve to the scrubber system in the plant. These pumps must have automated block valves on the suction and discharge. Operation of these valves should be managed such that the thermal expansion does not damage the pump.

A mistreated sealless pump can rupture with potentially serious results. The can can fail if valves on both sides of the pump are closed and the fluid in the pump expands either due to heating up from a cold condition or if the pump is started up. If the pump is run dry, the bearings can be ruined. The pump can heat up and be damaged if there is insufficient flow to take away heat from the windings. Sealless pumps, especially canned-motor pumps, produce a significant amount of heat, since nearly all the electrical energy lost in the system is absorbed by the fluid being pumped. *If this heat cannot be properly dissipated, the fluid will heat up with possibly severe consequences.* Considerable care must be used when installing a sealless pump to be sure that misoperations cannot occur.

The instrumentation recommended for sealless pumps may seem somewhat excessive. However, sealless pumps are expensive and they can be made to last for a long time, compared to conventional centrifugal pumps where seals may need to be changed frequently. Most failures of sealless pumps are caused by running them dry and damaging the bearings. Close monitoring of temperature is necessary in sealless pumps. Three temperature sensors (resistance temperature devices, or RTDs) are recommended: (1) in the internal fluid circulation loop, (2) in the magnet, or shroud, area, and (3) in the pump case area.

It is very important that sealless pumps be flooded with liquid before starting, to avoid damage to bearings from imbalance or overheating. Entrained gases in the suction can cause immediate imbalance problems and lead to internal bearing damage. Some type of liquid sensor is recommended. Sealless pumps must not be operated deadheaded (pump liquid full with inlet and/or outlet valves closed).

Properly installed and maintained, sealless pumps, both canned and magnetic-drive, offer an economical and safe way to minimize hazards and leaks of hazardous liquids.

Air Quality Regulatory Issues (Englund and Holden, 1995.) Environmental issues and regulations have developed from matters of secondary interest on the part of business to broad-ranging measures which affect the fundamental ways in which companies carry out the details of their business. The fast pace of development of environmental regulations and their changing, sometimes inconsistent requirements have made it difficult and expensive for companies to keep their facilities current. Many companies have adopted programs to keep them aware and abreast of continuing regulatory developments.

Although companies often fall under specific regulations pertaining only to their particular industry segments, a common thread running through a large number of manufacturing and commercial operations is the need to store materials considered to be toxic or hazardous. As a result, environmental regulations affecting the storage of toxic materials, either directly or indirectly, have had some of the most significant impacts on companies throughout the world in terms of both cost and operations. The Comprehensive Environmental Response, Compensation, and Liability Act of 1980, commonly known as Superfund, with its requirements to immediately report releases of reportable quantities of listed materials, has made the prevention of even minor spills, leaks, and releases from storage of toxic materials an important concern for owners. Also, storage and disposal of hazardous wastes are strictly and extensively regulated under the Resource Conservation and Recovery Act (RCRA) as amended in 1984.

In addition, restrictions on industrial air emissions under the Clean Air Act (CAA) as amended in 1977, the Clean Air Act Amendments (CAAA) of 1990, and other state and local statutes and regulations have universal impact on the storage of toxic materials, with direct and significant effects on the design and operation of toxic material storage facilities. Whereas the primary factors which once determined how air emissions from storage tanks were handled were fire protection and loss prevention, in recent years environmental protection concerns nearly always determine the extent and nature of the air emission controls required to be installed.

Permitting and Control Technology Requirements (*Air Quality Handbook,* 1988.) Almost any process equipment or facility that emits air pollutants will need to obtain an air emission permit from the appropriate local, state, or federal governmental authority before construction or modification begins. The application for the air emission permit generally must describe the pollutant-generating process to be installed or modified, along with any emission control equipment or techniques, state the emission rates of all pollutants emitted, support the statement of emissions with a technical analysis or study, and describe the way that the process and control equipment will be operated to comply with regulatory requirements.

In reviewing the permit application, the local, state, or federal permitting authority will normally evaluate the application for completeness, check the accuracy of calculations, analyze the stated emissions

for compliance with applicable regulations and environmental acceptability, and review the previous compliance history of the source and source owner. The source must operate within the bounds of the permit conditions in order to be considered in compliance with the permit. The source must still comply with all other air pollution laws, regulations, and ordinances, even if the permit conditions do not directly address them.

The process of evaluating air emission permit applications for large sources which are subject to federal permitting requirements is called New Source Review (NSR) and can be quite complicated, taking from six months to four years to complete. An NSR application would be required for a new source which could emit 100 tons per year or more of any criteria pollutant, after accounting for any air pollution control equipment.

The specific requirements to complete the NSR process will vary depending on the source location and characteristics, the federal and state regulations which apply, the compliance status of the facility if it is existing, and the nature of other sources in the area. Atmospheric dispersion modeling is often necessary to determine the maximum offsite ambient air concentrations of the various pollutants that will be emitted by the proposed new source or modification. All of the information in a permit application will normally be open to public scrutiny, including the details of the engineering study, except for specific process details that can be shown by the applicant to be trade secrets or proprietary business information. Nothing pertaining to the quality or quantity of air pollutant emissions can be claimed as proprietary.

The permitting requirements and procedures for a proposed NSR source are quite different, if the source is to be located in a nonattainment area for any of its major emitted pollutants, than if it is to be located in an attainment area. This usually increases the complexity of the permit application for such a source.

Federal Permitting in Nonattainment Areas If the source subject to NSR is to be located in an area which is nonattainment for any of the major pollutants that the source will emit, it will need to follow the federally approved state permitting requirements for nonattainment areas of that pollutant. In most such cases, offsetting emission reductions at the same or other source locations in the area so as to be at least equivalent to the allowed emission, increases at the proposed source must be provided.

HAZARDOUS MATERIALS AND CONDITIONS

REACTIVE CHEMICALS

General References: Bartknecht, *Dust Explosions,* Springer-Verlag, Berlin, 1989. Bartknecht, *Explosions Course Prevention, Protection,* Springer-Verlag, Berlin, 1981. Beever, "Hazards in Drying Thermally Unstable Powders," *Inst. Chem. Engr., Hazards X,* Symp. Ser. 115, 1989. Beever, "Scaling Rules for Prediction of Thermal Runaway," *Intl. Symp. on Runaway Reactions,* CCPS-AIChE. Cambridge, Mass., 1989. Beever and Thorne, "Isothermal Methods for Assessing Combustible Powders—Theoretical and Experimental Approach," *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Bowes, "A General Approach to the Prediction and Control of Potential Runaway Reaction," *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Bowes, *Self-heating: Evaluating and Controlling the Hazards,* Elsevier, 1984. *Bretherick's Reactive Chemical Hazards Database,* Version 2.0, Butterworth-Heinemann, Oxford, 1995. Brogli, Giger, Randegger, and Regenass, "Assessment of Reaction Hazards by Means of a Bench Scale Calorimeter," *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Brogli, Gygax, and Myer, "Differential Scanning Calorimetry—A Powerful Screening Method for the Estimation of the Hazards Inherent in Industrial Chemical Reactions," *Therm. Analy.,* 6th Symp., vol. 1, 549, 1980. Coates, "The ARC™ in Chemical Hazard Evaluation," *Chem. Ind.* **6:** 212, 1984. Coates, "The ARC™ in Chemical Hazard Evaluation," *Thermochim. Acta.* **85:** 369–372, 1984. Fenlon, "Calorimetric Methods Used in the Assessment of Thermally Unstable or Reactive Chemicals," *International Symposium for the Prevention of Major Chemical Accidents,* AIChE, 1987. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics,* Plenum Press, 1969. Grewer, "Direct Assessment and Scaling of Runaway Reaction and Decomposition Behavior Using Oven and DEWAR Tests," *Inst. Chem. Eng.,* Symp. Ser., 68, 1981. Grewer, "Use of DEWAR Calorimetry," *Proc. Runaway Chem. Reac. Haz. Symp.,* IBC, Amsterdam, November 1986. Halk, "SEDEX Versatile Instrument for Investigating Thermal Stability," *I. Chem. Eng.,* Symp. Ser. 68, 1981. Hub, "Adiabatic Calorimetry and SIKAREX Technique," *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Hub, "Experiences with the TSC 500 and RADEX Calorimeter," *Proc. Runaway Chem. Reac. Haz Symp.,* IBC, Amsterdam, November 1986. Hub, "Heat Balance Calorimetry and Automation of Testing Procedures," *Proc. Runaway Chem. Reac. Haz. Symp.,* IBC, Amsterdam, November 1986. *International Conference/Workshop on Modeling and Mitigating the Consequences of Accidental Releases of Hazardous Materials,* CCPS-AIChE, 1991. *International Conference on Hazard Identification and Risk Analysis, Human Factors and Human Reliability in Process Safety,* CCPS-AIChE, 1992. Kohlbrand, "Reactive Chemical Screening for Pilot Plant Safety," *Chem. Eng. Prog.* **81**(4): 52, 1985. Kohlbrand, "The Relationship Between Theory and Testing in the Evaluation of Reactive Chemical Hazards," *International Symposium for the Prevention of Major Chemical Accidents,* AIChE, 1987. Manufacturing Chemists Association, *Selected Case Histories,* Washington. D.C., 1951–1973. NFPA 491M, *Hazardous Chemical Reactions,* National Fire Protection Association, Quincy, Mass., 1991. Stull, "Fundamentals of Fire and Explosion," AIChE, 1976. Stull, "Linking Thermodynamics and Kinetics to Predict Real Chemical Hazards," *Loss Prevention,* AIChE, vol. 7, p. 67, 1976. Thomas, "Self Heating and Thermal Ignition—A Guide to Its Theory and Application," ASTM STP 502, ASTM, pp. 56–82, 1972. Townsend, "Accelerating Rate Calorimetry," *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Townsend and Kohlbrand, "Use of ARC™ to Study Thermally Unstable Chemicals and Runaway Reactions," *Proc. Runaway Chem. Reac. Haz. Symp.,* IBC, Amsterdam, November 1986. Townsend and Tou, "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter," *Thermochem. Acta.* **73:** 1–30 and references therein, 1980. Urben, Peter, ed. (Courtaulds), *Bretherick's Handbook of Reactive Chemical Hazards,* 5th ed., Butterworth-Heinemann, Oxford, 1994.

Understanding the Reactive Chemicals and Reactive Chemicals Systems Involved The main business of most chemical companies is to manufacture products through the control of reactive chemicals. The reactivity that makes chemicals useful can also make them hazardous. Therefore, it is essential that people who design or operate chemical processes understand the nature of the reactive chemicals involved.

Usually reactions are carried out without mishaps, but sometimes chemical reactions get out of control because of problems such as using the wrong raw material, using raw materials containing trace impurities, changed operating conditions, unanticipated time delays, equipment failure, or wrong materials of construction.

Such mishaps can be worse if the chemistry is not fully understood. A chemical plant can be *inherently safer* if knowledge of the chemistry of the process and the reactive chemicals systems involved is used in its design.

Reactive Hazard Review Reactive hazards should be evaluated using reviews on all new processes and on all existing processes on a periodic basis. There is no substitute for experience, good judgment, and good data in evaluating potential hazards. Reviews should include:

1. Review of process chemistry, including reactions, side reactions, heat of reaction, potential pressure buildup, and characteristics of intermediate streams
2. Review of reactive chemicals test data for evidence of flammability characteristics, exotherms, shock sensitivity, and other evidence of instability
3. Review of planned operation of process, especially the possibility of upsets, modes of failure, unexpected delays, redundancy of equipment and instrumentation, critical instruments and controls, and worst-credible-case scenarios

Worst-Case Thinking At every point in the operation, the process designer should conceive of the *worst* possible combination of circumstances that could *realistically* exist, such as loss of cooling water, power failure, wrong combination or amount of reactants, wrong valve position, plugged lines, instrument failure, loss of compressed air, air leakage, loss of agitation, deadheaded pumps, and raw-material impurities.

An engineering evaluation should then be made of the worst-case

consequences, with the goal that the plant will be safe even if the worst case occurs. A HAZOP study could be used to help accomplish worst-case thinking. When the process designers know what the worst-case conditions are, they should:

1. Try to avoid worst-case conditions.
2. Be sure adequate redundancy exists.
3. Identify and implement lines of defense.
   a. Preventive measures
   b. Corrective measures

Sometimes, as a last resort, it may be desirable to use a high degree of process containment or, possibly, abandon the process if the hazard is unacceptable.

It is important to note that the worst case should be something that is realistic, not something that is conceivable but extremely unlikely. The Dow Chemical Company has adopted the following philosophy for design scenarios in terms of independent causative effects:

1. All single events that can actually and reasonably occur are credible scenarios.
2. Scenarios that require the coincident occurrence of two or more totally independent events are not credible design scenarios.
3. Scenarios that require the occurrence of more than two events in sequence are not credible.
4. A failure that occurs while an independent device is awaiting repair represents but one failure during the time frame of the initiation of the emergency and is therefore credible. The lack of availability of the unrepaired device is a preexisting condition.

Reactive Chemicals Testing Much reactive chemical information involves thermal stability and the determination of (1) the temperature at which an exothermic reaction starts, (2) the rate of reaction as a function of temperature, and (3) heat generated per unit mass of material.

The evaluation of thermal stability requires the determination of the temperature at which an exothermic reaction occurs, the rate of such a reaction as a function of temperature, and the heat generated per unit mass of material by the reaction. In many cases, data on the increase of pressure during a reaction are also required, especially for vent sizing. The term *onset temperature* T_{onset} is used in two contexts:

1. In a testing context, it refers to the first detection of exothermic activity on the thermogram. The differential scanning calorimeter (DSC) has a scan rate of 10°C/min, whereas the accelerating rate calorimeter (ARC)* has a sensitivity of 0.02°C/min. Consequently, the temperature at which thermal activity is detected by the DSC can be as much as 50°C different from ARC data.
2. The second context is the process reactor. There is a potential for a runaway if the net heat gain of the system exceeds its total heat loss capability. A self-heating rate of 3°C/day is not unusual for a monomer storage tank in the early stages of a runaway. This corresponds to 0.00208°C/min, 10 percent of the ARC's detection limit. ARC data for the stored chemical would not show an exotherm until the self-heating rate was 0.02°C/min. Therefore, onset temperature information from ARC testing must be used with considerable caution.

Sources of Reactive Chemicals Data

Calculations Potential energy that can be released by a chemical system can often be predicted by thermodynamic calculations. If there is little energy, the reaction still may be hazardous if gaseous products are produced. Kinetic data is usually not available in this way. Thermodynamic calculations should be backed up by actual tests.

Differential Scanning Calorimetry (DSC) Sample and inert reference materials are heated in such a way that the temperatures are always equal. If an exothermic reaction occurs in the sample, the sample heater requires less energy than the reference heater to maintain equal temperatures. If an endothermic reaction occurs, the sample heater requires more energy input than the reference heater.

Onset-of-reaction temperatures reported by the DSC are higher than the true onset temperatures, so the test is mainly a screening test.

Differential Thermal Analysis (DTA) A sample and inert reference material are heated at a controlled rate in a single heating block. If an exothermic reaction occurs, the sample temperature will rise faster than the reference temperature. If the sample undergoes an endothermic reaction or a phase change, its temperature will lag behind the reference temperature.

This test is basically qualitative and can be used for identifying exothermic reactions. Like the DSC, it is also a screening test. Reported temperatures are not reliable enough to be able to make quantitative conclusions. If an exothermic reaction is observed, it is advisable to conduct tests in the ARC.

Mixing Cell Calorimetry (MCC) The MCC provides information regarding the instantaneous temperature rise resulting from the mixing of two compounds. Together, DSC and MCC provide a reliable overview of the thermal events that may occur in the process.

Accelerating Rate Calorimeter (ARC) The ARC can provide extremely useful and valuable data. This equipment determines the self-heating rate of a chemical under near-adiabatic conditions. It usually gives a conservative estimate of the conditions for and consequences of a runaway reaction. Pressure and rate data from the ARC may sometimes be used for pressure vessel emergency relief design. Activation energy, heat of reaction, and approximate reaction order can usually be determined. For multiphase reactions, agitation can be provided.

Nonstirred ARC runs may give answers that do not adequately duplicate plant results when there are reactants that may settle out or that require mixing for the reaction to be carried out (DeHaven and Dietsche, The Dow Chemical Company, Pittsburgh, Calif., "Catalyst Explosion: A Case History," *Plant Operations Progress*, April 1990).

An example of data from an ARC run is shown in Fig. 26-29.

Vent Sizing Package (VSP) The VSP is an extension of ARC technology. The VSP is a bench-scale apparatus for characterizing runaway chemical reactions. It makes possible the sizing of pressure relief systems with less engineering expertise than is required with the ARC or other methods.

Reactive System Screening Tool (RSST) The RSST is a calorimeter that quickly and safely determines reactive chemical hazards. It approaches the ease of use of the DSC with the accuracy of the VSP. The apparatus measures sample temperature and pressure within a sample containment vessel. The RSST determines the potential for runaway reactions and measures the rate of temperature and pressure rise (for gassy reactions) to allow determinations of the energy and gas release rates. This information can be combined with simplified methods to assess reactor safety system relief vent requirements. It is especially useful when there is a need to screen a large number of different chemicals and processes.

Shock Sensitivity Shock-sensitive materials react exothermically when subjected to a pressure pulse. Materials that do not show an exotherm on a DSC or DTA are presumed not to be shock sensitive. Testing methods include:

- *Drop weight test.* A weight is dropped on a sample in a metal cup. The test measures the susceptibility of a chemical to decompose explosively when subjected to impact. Weight and height can be varied to give semiquantitative results for impact energy. This test should be applied to any materials known or suspected to contain unstable atomic groupings.
- *Confinement cap test.* Detonatability of a material is determined using a blasting cap.
- *Adiabatic compression test.* High pressure is applied rapidly to a liquid in a U-shaped metal tube. Bubbles of hot compressed gas are

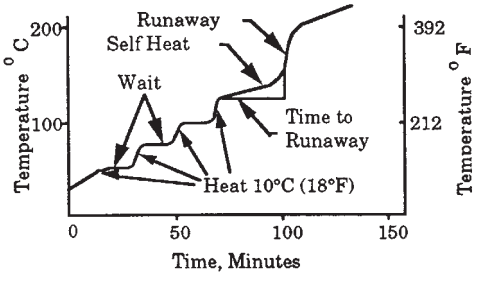


FIG. 26-29 Operation of the ARC.

* ARC is the trademark of Columbia Scientific Industries Corporation.

driven into the liquid and may cause explosive decomposition of the liquid. This test is intended to simulate water hammer and sloshing effects in transportation, such as humping of railway tank cars. It is very severe and gives worst-case results.

Flammability–Flash Point The closed-cup flash point determination produces the most important data to determine the potential for fire. The flash point is the lowest temperature at which the vapors can be ignited under conditions defined by the test apparatus and method.

Flammable Limits Flammable limits, or the flammable range, are the upper and lower concentrations (in volume percent) which can just be ignited by an ignition source. Above the upper limit and below the lower limit no ignition will occur. Data are normally reported at atmospheric pressure and at a specified temperature. Flammable limits may be reported for atmospheres other than air and at pressures other than atmospheric.

Autoignition Temperature The autoignition temperature of a substance, whether liquid, solid, or gaseous, is the minimum temperature required to initiate or cause self-sustained combustion in air, with no other source of ignition. Autoignition temperatures should be considered only as approximate. Test results tend to give temperatures that are higher than the actual autoignition temperature.

Dust Explosions Combustible, dusty materials, with particle sizes less than approximately 200 mesh, can explode if a sufficient concentration in air is present along with an ignition source. The standard test has been designed to determine rates of pressure rise during an explosion, the maximum pressure reached, and the minimum energy needed to ignite the material. These data are useful in the design of safe equipment to handle dusty combustible materials in a process. Combustible dusts need a minimum volume to develop their full reaction velocity. Bartknecht states that for determination of explosion data of combustible dusts, a minimum volume of 16 L (4.23 gal) would be required to ensure correlation with data from large test vessels (Bartknecht, 1981, p. 39). This has been confirmed by comprehensive testing with a 20-L (5.28-gal) sphere.

Unstable Compounds (Bretherick, L., British Petroleum Co. Ltd., *Handbook of Reactive Chemical Hazards,* 4th ed., Butterworths, London, pp. S1–S23, 1990, by permission of Butterworth-Heinemann and L. Bretherick; note that the 5th ed. is available in electronic format from *Bretherick's Reactive Chemical Hazards Database,* Version 2.0, Butterworth-Heinemann, Oxford, 1995.) Explosibility may be defined as the tendency of a chemical system (involving one or more compounds) to undergo violent or explosive decomposition under appropriate conditions of reaction or initiation. It is of great interest to be able to predict which compound or reaction systems are likely to exhibit explosability, and much work has been devoted to this end. The contributions of various structural factors (bond-groupings) have been evaluated in terms of heats of decomposition and oxygen balance of the compound or compounds involved in the system. Oxygen balance is the difference between the oxygen content of the chemical compound and that required to fully oxidize the carbon, hydrogen, and other oxidizable elements in the compound. Materials or systems approaching zero oxygen balance give the maximum heat release and are the most powerfully explosive.

Most chemical reactions are exothermic. In the few endothermic reactions that are known, heat is absorbed into the reaction product or products, which are known as endothermic or energy-rich compounds. Such compounds are thermodynamically unstable because heat would be released on decomposition of their elements. The majority of endothermic compounds possess a tendency toward instability and possibly explosive decomposition under various circumstances of initiation.

Following are the classes of compounds that have a tendency to undergo violent or explosive decomposition.

Acetylenic compounds
Alkyl hydroperoxides, peroxyacids
Aminachromium peroxocomplexes
Ammonium perchlorates
Arenediazoates
Azides (acyl, halogen, nonmetal, organic)
Bis-arenediazo sulfides
Acyl or alkyl nitrates
Alkyl perchlorates
Aminemetal oxosalts
Arenediazo aryl sulfides
Arenediazoniumolates
Azo compounds
Chlorite salts
Diazirines
Diazonium carboxylates or salts
Difluoramino compounds
Fluorodinitromethyl compounds
Haloacetylene derivatives
Halogen azides
High-nitrogen compounds
Hydroxylammonium salts
Metal acetylides
N,N,N-trifluoroalkylamidines
N-halogen compounds
N-metal derivatives
Nitroalkanes, *c*-nitro, and polynitroaryl compounds
Oxosalts of nitrogeneous bases
Perchloryl compounds
Poly(dimercuryimmonium salts)
Tetrazoles
Trinitroethyl orthoesters
Diazo compounds
Diazonium sulfides and derivatives, Xanthates
1,2-epoxides
Halo-aryl metals
Haloarenemetal π-complexes
Halogen oxides
Hydrazinium salts
Hypohalites
Metal fulminates or *aci*-nitro salts oximates
N-azolium compounds
N-haloimides
N-nitro compounds
Nitroso compounds
Perchloric acid
Peroxides, (cyclic, diacyl, dialkyl), Peroxyesters
Polynitroalkyl compounds
Triazenes

COMBUSTION AND FLAMMABILITY HAZARDS

General References: Bartknecht, *Explosions Course Prevention Protection,* Springer-Verlag, Berlin, 1981. Bartknecht, *Dust Explosions,* Springer-Verlag, Berlin, 1989. Beneditti, ed., *Flammable and Combustible Liquids Code Handbook,* 3d ed., based on NFPA 30, *Flammable and Combustible Liquids Code and Automotive and Marine Service Station Code,* National Fire Protection Association, Quincy, Mass., 1987. Bodurtha, Engineering Dept., Du Pont, *Industrial Explosion Prevention and Protection,* McGraw-Hill, 1980. Cawse, Pesetsky, and Vyn, *The Liquid Phase Decomposition of Ethylene Oxide,* Union Carbide Corporation, Technical Center, South Charleston, W.Va. *CPQRA (Guidelines for Chemical Process Quantitative Risk Analysis),* CCPS-AIChE, New York, 1989. Crowl and Louvar, *Chemical Process Safety: Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, N.J., 1990. DiNenno, P. J. (ed.), *SPFE Handbook of Fire Protection Engineering,* 1st ed., National Fire Protection Association, Quincy, Mass., 1988. Drysdale, *An Introduction to Fire Dynamics,* Wiley, Suffolk, 1985. *Fire Safety Data,* Fire Protection Association, London 1980. *Guidelines for Engineering Design for Process Safety,* CCPS-AIChE, 1993. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980. Stull, *Fundamentals of Fire and Explosion,* New York, 1976.

Introduction The enchanting flame has held a special mystery and charm the world over for thousands of years. According to Greek myth, Prometheus the Titan stole fire from the heavens and gave it to mortals—an act for which he was swiftly punished. Early people made use of it anyway. Soon the ancients came to regard fire as one of the basic elements of the world. It has since become the familiar sign of the hearth and the mark of youth and blood—as well as the object of intense curiosity and scientific investigation.

Suitably restrained, fire is of great benefit; unchecked or uncontrolled, it can cause immense damage. We respond to it with a powerful fascination coupled with an inbred respect and fear. A good servant but a bad master is Thoreau's "most tolerable third party" (Cloud, "Fire, the Most Tolerable Third Party," *Michigan Natural Resources,* May-June 1990).

What Is Fire? (DiNenno, 1988.) Fire or combustion is normally the result of fuel and oxygen coming together in suitable proportions and with a source of heat. The consumption of a material by a fire is a chemical reaction in which the heated substance combines with oxygen. Heat, light, smoke, and products of combustion are generated. The net production of heat by a fire involves both heat-producing and heat-absorbing reactions, with more heat being produced than is absorbed.

A flame is a rapid self-sustaining chemical reaction that occurs in a distinct reaction zone. Two basic types of flame are (1) the diffusion flame, which occurs on ignition of a fuel jet issuing into air, and for which the limiting rate is controlled by diffusion, and (2) the aerated, or premixed, flame, which occurs when fuel and air are premixed before ignition, and for which the limiting rate is controlled by reaction kinetics. The main concern in fire applications is with diffusion flames, as contrasted to premixed flames where fires and oxidants are premixed or brought together to the combustion region. At high turbulence in diffusion flames, kinetics and diffusion may be of roughly equal importance. Combustion is self-propagating; burning materials

produce heat, which causes more of the solid to produce flammable vapors until either the fuel or oxygen is exhausted, or until the fire is extinguished in some other way (*API Recommended Practices,* 3d ed., Practice 521, November 1990).

Energy in the form of heat is required:

1. To produce vapors and gases by vaporization or decomposition of solids and liquids. Actual combustion usually involves gases or vapors intimately mixed with oxygen molecules.
2. To energize the molecules of oxygen and flammable vapors into combining with one another and so initiating a chemical reaction.

The amount of energy needed to cause combustion varies greatly. Hydrogen and carbon disulfide can be ignited by tiny sparks or simply by static generated as the gases or vapors discharge from pipes into air. Other materials, such as methylene chloride, require such large amounts of energy to be ignited that they are sometimes considered nonflammable.

Fire can also result from the combining of such oxidizers as chlorine and various hydrocarbon vapors; oxygen is not required for a fire to take place.

Ordinarily, combustible solids do not combine directly with oxygen when they burn. They give off vapor and gaseous decomposition products when they are heated, and it is the vapors or gases which actually burn in the characteristic form of flames. Thus, before a solid can be ignited it must be heated sufficiently for it to give off flammable concentrations of vapors. There are exceptions to the general rule that a solid must vaporize or decompose to combine with oxygen; some finely divided materials such as aluminum powder and iron powder can burn and it is probable that they do not vaporize appreciably before burning. Some metallic dusts will explode in air by light radiation alone without conduction and convection (Bartknecht, 1989, p. 14).

Products of Combustion Heat, light, smoke, and asphyxiating and toxic gases are produced by fire. In a hot, well-ventilated fire, combustion is usually nearly complete. Nearly all the carbon is converted to carbon dioxide, all the hydrogen to steam, and oxides of various other elements such as sulfur and nitrogen are produced.

This is not the case in most fires where some of the intermediate products, formed when large, complex molecules are broken up, persist. Examples are hydrogen cyanide from wool and silk, acrolein from vegetable oils, acetic acid from timber or paper, and carbon or carbon monoxide from the incomplete combustion of carbonaceous materials. As the fire develops and becomes hotter, many of these intermediates, which are often toxic, are destroyed—for example, hydrogen cyanide is decomposed at about 538°C (1000°F).

Small airborne particles of partially burnt carbonaceous materials from smoke, which is often made more opaque by steam from combustion or from water added to the fire, may be formed when there is only partial combustion of fuel.

Many hydrocarbon flames are luminous because of the incandescent carbon particles formed in the flames. Under certain conditions, these particles are released from the luminous flames as smoke. Smoke from hydrocarbons is usually formed when the system is fuel rich, either overall or locally.

Common materials—such as textiles in the form of fibers or fabrics, foamed rubber, foamed plastics, thin sheets of plastic, paper, corrugated cardboard, combustible dusts, dry grass and twigs, and wood shavings—are all examples of materials with large surface areas in relation to their volumes. In a well-established fire, materials with relatively small surface areas, such as chunks of coal or logs, burn readily.

Combustible Dusts Dusts are particularly hazardous; they have a very high surface area–to–volume ratio. When finely divided as powders or dusts, solids burn quite differently from the original material in the bulk. Dust and fiber deposits can spread fire across a room or along a ledge or roof beam very quickly. On the other hand, accumulations of dust can smolder slowly for long periods, giving little indication that combustion has started until the fire suddenly flares up, possibly when no one suspects a problem.

Many combustible dusts produced by industrial processes are explosible when they are suspended as a cloud in air. A spark may be sufficient to ignite them. After ignition, flame spreads rapidly through the dust cloud as successive layers are heated to ignition temperature. The hot gases expand and produce pressure waves, which travel ahead of the flame. Any dust lying on surfaces in the path of the pressure waves will be thrown into the air and could cause a secondary explosion more violent and extensive than the first.

Liquids A vapor has to be produced at the surface of a liquid before it will burn. Many common liquids give off a flammable concentration of vapor in air without being heated, sometimes at well below room temperature. Gasoline, for example, gives off ignitable vapors above about –40°C (–40°F), depending on the blend. The vapors are easily ignited by a small spark or flame. The reason there are not many fires in automobile gasoline tanks is that the vapor space above the gasoline is almost always above the upper flammability limit. Other liquids, such as fuel oil and kerosene, need to be heated until sufficient vapor is produced to produce a flammable concentration.

For any flammable vapor there are maximum and minimum concentrations of vapor in air beyond which it cannot burn. When the concentration of vapor in air is too low, there is insufficient fuel for burning; when it is too high, there is insufficient oxygen for burning.

If the density of a vapor is greater than air, as is the case with most gases and vapors encountered in industry, flammable concentrations may collect at low levels, such as at floor level or in basements, and can travel considerable distances to a source of ignition and the flames will then flash back.

Gases Flammable gases are usually very easily ignited if mixed with air. Flammable gases are often stored under pressure, in some cases as a liquid. Even small leaks of a liquefied flammable gas can form relatively large quantities of gas, which is ready for combustion.

Transparent (Invisible) Flames Some materials have nearly nonluminous flames, which may not be visible, especially in the daytime. For example, hydrogen has a nearly nonvisible flame in the daytime. A person may walk unaware into a hydrogen leak flame. Some other materials, including some alcohols such as methanol, also have nearly nonluminous flames and may be unusually hazardous because the flames cannot be seen in the daytime.

The Fire Triangle The well-known *fire triangle* (see Fig. 26-33) is used to represent the three conditions necessary for a fire: (1) fuel, (2) oxygen or other oxidizer (a gaseous oxidizer such as chlorine, a liquid oxidizer such as bromine, or a solid oxidizer such as sodium bromate), and (3) heat (energy).

If one of the conditions in the fire triangle is missing, fire does not occur, and if one is removed, fire is extinguished. Usually a fire occurs when a source of heat contacts a combustible material in air, and then the heat is supplied by the combustion process itself.

The fire triangle indicates how fires may be fought or prevented:

1. Cut off or remove the fuel.
2. Remove the heat—usually done by putting water on the fire.
3. Remove the supply of oxygen—usually done by foam or inert gas.

Stoichiometric Concentration (Used by permission of Frank T. Bodurtha, Inc., New London, New Hampshire). In a combustion reaction in air, the stoichiometric concentration, C_{st}, of any reactant is the concentration theoretically required for complete conversion by reacting completely with oxygen. For example, for the combustion of propane in air:

$$\underset{\text{——Air——}}{C_3H_8 + 5O_2 + 18.8N_2} \rightarrow 3CO_2 + 4H_2O + 18.8N_2$$

$$C_{st} \text{ for propane} = \left(\frac{1}{1+5+18.8}\right)100 = 4.0\% \text{ (volume)}$$

Moles at start = 24.8; moles after combustion = 25.8.

The change in moles upon the combustion of propane and many other hydrocarbons is either zero or small. Usually, pressure rise in the combustion of a vapor or gas is due mainly to change in temperature, not change in moles.

The C_{st} for a flammable solid may also be calculated. For sugar, whose molecular weight is 342, C_{st} is calculated as follows:

$$\underset{\text{—Sugar—}}{C_{12}H_{22}O_{11}} + \underset{\text{——Air——}}{12O_2 + 46.4N_2} \rightarrow 12CO_2 + 11H_2O + 46.4N_2$$

58.4 volumes 69.4 volumes

TABLE 26-10 Flammability Limits, Autoignition Temperature, and Flash Points of Selected Substances in Air at Atmospheric Pressure

Chemical compound	Flam. limits, lower, % v/v	Flam. limits, upper, % v/v	Autoignition temperature, °C	Flash point, closed cup, °C	Flash point, open cup, °C
Acetone	2.6	13	465	–18	–9
Acetylene	2.5	100	305	—	—
Ammonia	15	28	651°	—	—
Benzene	1.4°	8.0°	562°	–11	—
n-Butane	1.8	8.4	405	–60	—
Carbon disulfide	1.3	50	90	–30	—
Carbon monoxide	12.5	74	—	—	—
Cyclohexane	1.3	7.8	245	–20	—
Ethane	3.0	12.4	515	–135	—
Ethylene	2.7	36	490	–121	—
Ethylene dichloride	6.2°	15.9°	413°	13	18
Ethylene oxide	3°	100°	429°	—	–20
Hydrogen	4	75	400	—	—
Methane	5	15	540	—	—
Propane	2.1	9.5	450	<–104	—
Propylene	2.4	11	460	–108	—
Styrene	1.1°	6.1°	490°	32	38
Toluene	1.3°	7.0°	536°	4	7
Vinyl chloride	4°	22°	472°	—	–78

°Factory Mutual Engineering Corporation, 1967.

SOURCES: Lees, 1980.

Flammability limits and autoignition temperatures: Zabetakis, *Bureau of Mines Bulletin 627,* except where given in footnotes.

Flash points: Factory Mutual Engineering Corporation, 1967.

$$C_{st} = \frac{(342)(1000)}{(12 + 46.4)(22.4)(298/273)} = 239.5 \text{ mg/L air at } 25°\text{C}$$

Table 26-10 shows flammability limits, autoignition temperature, and flash points of selected substances in air at atmospheric pressure.

Burning in Pure Oxygen The flammability of a substance depends strongly on the partial pressure of oxygen in the atmosphere. Increasing oxygen content affects the lower flammability limit only slightly, but it has a large effect on the upper flammability limit. Increasing oxygen content has a marked effect on the ignition temperature (reduces it) and the burning velocity (increases it). Use of air enriched with oxygen, or pure oxygen, can greatly increase the hazards of combustion reactions.

Burning in Other Oxidizable Atmospheres Chemically, oxygen is not the only oxidizing agent, though it is the most widely recognized and has been studied the most. Halogens are examples of oxidants that can react exothermically with conventional fuels and show combustion behavior. The applicability of flammability limits applies to substances that burn in chlorine. Chlorination reactions have many similarities to oxidation reactions. They tend not to be limited to thermodynamic equilibrium and often go to complete chlorination. The reactions are often highly exothermic. Chlorine, like oxygen, forms flammable mixtures with organic compounds. Flames can also propagate in mixtures of oxides of nitrogen and other oxidizable substances.

Flame Quenching Flame propagation is suppressed if the flammable mixture is held in a narrow space. If the space is sufficiently narrow, flame propagation is suppressed completely. The largest diameter at which flame propagation is suppressed is known as the *quenching diameter.* For an aperture of slotlike cross section, there is a critical slot width. The term *quenching distance* is sometimes used as a general term covering both quenching diameter and critical slot width and sometimes meaning only the latter.

There is a maximum safe gap measured experimentally which will prevent the transmission of an explosion occurring within a container to a flammable mixture outside the container. Critical and maximum experimental safe gaps for a number of materials in air are listed in Lees (1980, pp. 491–492). These quenching effects are important in the design of flame arresters and flameproof equipment.

Heterogeneous Mixtures (Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors,* Bulletin 627, Bureau of Mines, 1965.) Heterogeneous (poorly mixed) gas phase mixtures can lead to fires that normally would be totally unexpected. It is important to recognize that heterogeneous mixtures can ignite at concentrations that would normally be nonflammable if the mixture were homogeneous. For example, 1 L of methane can form a flammable mixture with air at the top of a 100-L container, although the mixture would contain only 1.0 percent methane by volume. This would be below the lower flammable limit if complete mixing occurred at room temperature and the mixture would not be flammable. This is an important concept since *layering* can occur with any combustible gas or vapor in both stationary and flowing mixtures.

Heterogeneous mixtures are formed, at least for a short time, when two gases or vapors are first brought together.

Explosions in the Absence of Air Some gases with positive heats of formation can be decomposed explosively in the absence of air. Ethylene reacts explosively at elevated pressure and acetylene at atmospheric pressure in large-diameter piping. Heats of formation of these materials are +52.3 and +227 kJ/mol (+22.5 and +97.6 × 10^3 Btu/lb mol), respectively.

Explosion prevention can be practiced by mixing decomposable gases with inert diluents. For example, acetylene can be made nonexplosive at a pressure of 100 atm (10.1 MPa) by including 14.5 percent water vapor and 8 percent butane (Bodurtha, 1980). One way to prevent the decomposition reaction of ethylene oxide vapor is to use methane gas to blanket the ethylene oxide liquid.

GAS EXPLOSIONS

GENERAL REFERENCES: Bartknecht, *Explosions,* Springer-Verlag, New York, 1981. Bodurtha, *Industrial Explosion Prevention and Protection,* McGraw-Hill, New York, 1980. Coward and Jones, "Limits of Flammability of Gases and Vapors," *U.S. Bur. Mines Bull. 503* (USNTIS AD-710 575), 1952. Lees, *Loss Prevention in the Process Industries,* vols. 1 and 2, Butterworths, London, 1980. National Fire Protection Association, *Explosion Prevention Systems,* NFPA 69, Quincy, Mass. National Fire Protection Association, *Venting of Deflagrations,* NFPA 68, Quincy, Mass. Zabetakis, "Flammability Characteristics of Combustible Gases and Vapors," *U.S. Bur. Mines Bull. 627* (USNTIS AD-710 576), 1965. NOTE: *NFPA reviews, and may change, its standards and guides periodically. Always check the latest edition.*

Fuel and Oxygen

Flash Point and Flammable Limits Flash points and flammable limits in percent by volume have been tabulated by the National Fire Protection Association (NFPA) (National Fire Protection Association, *Fire Hazard Properties of Flammable Liquids, Gases, and*

Volatile Solids, NFPA 325, Quincy, Mass.). Pressure particularly affects flash point and the *upper flammable limit* (UFL); see later section entitled "Effect of Temperature, Pressure, and Oxygen." Mists of high-flash-point liquids may be flammable; the *lower flammable limit* (LFL) of fine mists and accompanying vapor is about 48 g/m^3 of air, basis 0°C and 1 atm (0.048 oz/ft^3).

For practical purposes, LFL is the same as *lower explosive limit* (LEL). (Ignitability limits depend upon the strength of the ignition source; the ignitability range for relatively weak ignition sources is less than the flammable range.) LFLs in percent by volume generally decrease as molecular weight increases.

The equilibrium vapor pressure of a flammable liquid at its closed-cup flash point about equals its LFL in percent by volume. Thus, the vapor pressure of toluene at its closed-cup flash point (4.4°C or 40°F) of 1.2 percent (1.2 kPa) is close to its LFL of 1.1 percent. The composite LFL of a mixture may be estimated by Le Chatelier's Rule:

$$\text{Composite LFL (\% by vol.)} = \frac{100}{C_1/\text{LFL}_1 + C_2/\text{LFL}_2 + \cdots + C_n/\text{LFL}_n} \tag{26-43}$$

where the *C*s are percentages of volume of total fuel, i.e., without air or inert gas. As shown in Table 26-11, the indicated mixture is flammable even though each component is below its LFL. The composite LFL stays the same if the concentration of each component is multiplied by the same number. Composite upper flammable limits may be approximated similarly.

The concentration of fuel in air in a process should be maintained at or below 25 percent of the LFL, with automatic instrumentation and safety interlocks; however, up to 60 percent of LFL is permitted by the NFPA—except for ovens or furnaces. (Ovens and furnaces are covered in NFPA 86.)

Limiting Oxidant Concentration (LOC) It is often prudent to base explosion prevention on inerting. The LOC is the concentration of oxidant—normally oxygen—below which a fuel-oxidant explosion cannot occur. (The LOC is also called MOC, the minimum oxygen for combustion.) With adequate depletion of oxygen, an explosion cannot occur *whatever the concentration of fuel.* Nevertheless, in these circumstances a fuel–air–inert gas mixture may become flammable if sufficient air is added. Many LOCs are given in NFPA 69. In general, organic flammable gases or vapors will not propagate flame in mixtures of the organic, added nitrogen, and air below about 10.5 percent by volume O_2 at 1 atm and near normal room temperature. Hydrogen (LOC = 5 percent) and some other inorganic gases have lower LOCs.

For LOCs of 5 percent and greater, the O_2 concentration should not exceed 60 percent of the LOC, but with continuous monitoring the O_2 may be kept 2 percent below the LOC (NFPA 69, 1992). Neutronics, Inc., of Exton, Pennsylvania, supplies an inerting control system that has had wide application in many industries.

Explosion prevention by inerting has several advantages over explosion protection techniques, such as explosion venting. For example, with successful inerting, fires or business interruptions cannot occur. Nevertheless, beware of the potential of asphyxiation with inerting; proper vessel entry procedures must be implemented and occasionally it may be prudent to monitor for oxygen in workplaces.

Effect of Temperature, Pressure, and Oxygen LFLs and LOCs at 1 atm decrease about 8 percent of their values at near normal room temperature for each 100°C increase. Upper flammable limits increase approximately 8 percent for the same conditions.

TABLE 26-11 Le Chatelier's Rule

	Concentration, vol %	C, %	LFL, vol %
Hexane (1)	0.8	24.2	1.1
Methane (2)	2.0	60.6	5.0
Ethylene (3)	0.5	15.2	2.7
Total fuel	3.3		
Air	96.7		

$$\text{Composite LFL} = \frac{100}{24.2/1.1 + 60.6/5.0 + 15.2/2.7} = 2.5 \text{ vol \%}$$

Pressure affects flash point. A decrease in pressure lowers the flash point. With toluene, for example, at two-thirds of an atmosphere the vapor pressure must be only 0.74 kPa (5.6 mm Hg) to equal the LFL of 1.1 percent. (No significant difference in LFL will exist at two-thirds of an atmosphere compared to the published LFL of 1.1 percent at one atmosphere.) This vapor pressure occurs at −3°C, corresponding to a decrease in flash point of about 7.4°C from one atmosphere. Conversely, an increase in pressure raises the flash point.

Pressure also affects flammable limits. A decrease in pressure to about one-half atmosphere does not affect the flammable range significantly. At lower pressure the flammable range narrows and the flammable limits may disappear below about 6.7 kPa (50 mm Hg). An increase in pressure lowers LFLs and LOCs on a volume basis only slightly. But on a *weight basis,* LFLs are proportional to the absolute pressure. For example, the LFL of hexane is 43 g/m^3 (0.043 oz/ft^3) air at 1 atm, basis 0°C, but it is 86 g/m^3 air (0.086 oz/ft^3) at 2 atm. An increase in pressure increases UFLs greatly. The effect of elevated pressure on LFLs, LOCs, and UFLs for ethane is tabulated in Table 26-12. Based on tests by the U.S. Bureau of Mines, UFLs at high pressure and near normal room temperatures may be *estimated* by

$$\text{UFL}_p = \text{UFL} + 20.6\,(\log_{10} P + 1) \tag{26-44}$$

where UFL_p (percent by volume) is at the elevated absolute pressure, P is in megapascals absolute (MPa), and UFL (percent by volume) is at 1 atm. LFLs are about the same in oxygen as in air, since oxygen in air is in excess for combustion at LFL, but UFLs increase markedly in oxygen compared to air, as shown by the examples in Table 26-13. For organic substances, UFLs at 1 atm are about 48 percent higher in oxygen than in air. Moreover, the *minimum ignition energies* (MIE) in oxygen are about 1/100 of the MIEs in air, so vapors in oxygen are extraordinarily easy to ignite.

Ignition Sources Normally it is best practice not to base explosion safety solely on the presumed absence of an ignition source. Explosion control should be based on prevention or protection techniques, or both. Even so, all reasonable measures should be taken to eliminate ignition sources.

TABLE 26-12 Effect of Elevated Pressure on LFL, LOC, and UFL of Ethane*†

Pressure MPa gauge,	psig	LFL, vol %	% decrease in LFL	LOC, vol %	% decrease in LOC	UFL, vol %	% increase in UFL
0	(0)	2.85	—	11.0	—	12.3	
0.69	(100)	2.80	1.75	—	—	30.0	144
1.72	(250)	2.70	5.20	9.3	15.5	40.0	225
3.45	(500)	2.55	10.5	8.9	19.1	47.0	282
5.17	(750)	2.40	15.8	—	—	50.0	306
6.20	(900)	—	—	8.8	20.0		
6.90	(1000)	2.20	22.8	—	—	51.5	319

*Nitrogen as inert gas. Near normal room temperature. % decrease and increase is from 0 MPa gauge.

†After Kennedy, Spolan, Mock, and Scott, "Effect of High Pressures on the Explosibility of Mixtures of Ethane, Air and Carbon Dioxide, and of Ethane, Air and Nitrogen," *U.S. Bureau of Mines Report Invest.,* 4751, 1950.

TABLE 26-13 Flammability Limits in Air and Oxygen at Ordinary Temperatures and 1 atm*

	LFL in air, vol %	LFL in O_2, vol %	UFL in air, vol %	UFL in O_2, vol %	Δ UFL, vol %
Butane	1.9	1.8	8.5	49	40.5
1-Butene	1.6	1.8	9.3	58	48.7
Ethane	3.0	3.0	12.5	66	53.5
Ethylene	3.1	3.0	32	80	48
Isopropyl ether	—	—	21	69	48
Methane	5.3	5.1	14	61	47
Propane	2.2	2.3	9.5	55	45.5
Vinyl chloride	4.0	4.0	22	70	48

*Based on Coward and Jones, "Limits of Flammability of Gases and Vapors," *U.S. Bureau of Mines Bulletin 503* (USNTIS AD-701575), 1952.

Autoignition The minimum autoignition temperature (AIT) of a substance is the minimum temperature at which vapors ignite spontaneously from the heat of the environment. (Flash points are lower than minimum autoignition temperatures; in flash-point tests an open flame is used as an igniter.) The ignition temperature found in NFPA 325 is the same as minimum autoignition temperature. A method for determination of autoignition temperatures is given in E659, *Standard Test Method for Autoignition Temperatures of Liquid Chemicals,* of the American Society for Testing and Materials (ASTM). Autoignition depends on many factors—namely, ignition delay, concentration of vapors, environmental effects (volume, pressure, and oxygen content), catalytic material, and flow conditions. Based on a development by A. Beerbower, Exxon Research and Engineering, for the effect of volume on AIT (see Coffee, "Cool Flames and Autoignitions: Two Oxidation Processes," *Chem. Eng. Prog. 13th Loss Prev. Symp.,* Houston, 1979, pp. 79–82):

$$t_a = \frac{(t_d - 75)(15 - \log_{10} V_a)}{(15 - \log_{10} V_d)} + 75 \qquad (26\text{-}45)$$

where t_a (°C) = minimum AIT for volume V_a (mL)
t_d (°C) = minimum AIT as measured in volume V_d (mL)

For a plant vessel of 3.785×10^6 mL (1000 U.S. liquid gallons) and $t_d = 330$°C in a 500-mL test vessel (ASTM E659), $t_a = 249$°C, i.e., 81°C less than measured in the 500-mL flask.

As a guide, because of convection that occurs from hot surfaces, ignition by a hot surface in open air should not be assumed unless the surface temperature is at least 200°C above the published minimum autoignition temperature (American Petroleum Institute, *Ignition Risk of Hot Surfaces,* API PSD 2216, Washington, 1980).

Autooxidation Autooxidation—spontaneous ignition—is the phenomenon of self-heating by slow oxidation with accompanying evolution of heat, leading to ignition when the heat of oxidation cannot be dissipated adequately. Thermal insulation or rags wet with oils or other organic liquids susceptible to oxidation have caused serious fires. A fire may occur even if the hot surface is below the minimum AIT. Relatively high flash-point materials are most susceptible to autooxidation; low-flash-point materials may evaporate without ignition. Leaks that may contaminate insulation should be eliminated or diverted away from insulation to the extent feasible. Thermal insulation known to be wetted with oil or other high-boiling organic fluids should be removed promptly and replaced.

Compression Adiabatic compression results in high temperatures determined by the compression and specific heat ratios, as shown in Eq. (26-46):

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} \qquad (26\text{-}46)$$

where the subscript 2 refers to the final state, T is the absolute temperature, P is the absolute pressure, and k is the ratio of specific heats.

Various types of rapid, adiabatic compressions have caused explosions. With propane at an initial temperature of 25°C, T_2 = 432°K (159°C) for compression and specific heat ratios of 25 and 1.13, respectively. Assume that now air enters a compressor to bring propane into the flammable range at 5 percent by volume. The mixture then will be mostly air with $k = 1.47$. The same compression ratio of 25 will elevate the final temperature T_2 to 834°K (561°C), i.e., above the published autoignition temperature of 450°C for propane and perhaps high enough to cause an explosion.

Other Ignition Sources Hazardous classification of locations for electrical installations is covered in Articles 500–504 of the *National Electrical Code* (NEC) (NFPA 70). Proper hazardous classification is essential for safety and for prevention of explosion and fire losses. Class 1 in the NEC is for vapors and gases; in the United States, in brief, Division 1 of Class 1 includes those locations where flammable concentrations exist continuously or frequently. Division 2 includes locations where flammable concentrations may exist only in case of accidental escape of vapors or gases, or in case of abnormal operation of equipment. Static electricity, which causes fires and explosions with flammable vapors and gases, is covered later in Sec. 26. Other ignition sources include friction and impact plus rubbing; with rubbing beware of metal-to-metal contact where heat cannot be conducted away. Even with grounded equipment, *hydrogen may ignite spontaneously,* often, for instance, when it exits a stack or leaks out of a pipe. (The minimum ignition energy of hydrogen is about 0.02 mJ, approximately 1/10 of the MIEs for paraffin hydrocarbons.)

Explosion Pressure An *explosion* is the action of "going off" with a loud noise under the influence of suddenly developed internal energy. Thus, an explosion is a result, not a cause. Deflagrations and detonations cause chemical explosions. A *deflagration* is a reaction that propagates to the unreacted material at a speed less than the speed of sound in the unreacted material. A *detonation* is a reaction that propagates to the unreacted material at a speed greater than the speed of sound in the unreacted material; it is accompanied by a shock wave and inordinately high pressure.

Deflagration Pressure The increase in pressure in a vessel from a deflagration results from an increase in temperature; the actual maximum flame temperature for propane, for example, is 1925°C (3497°F). No significant increase in moles of gas to cause pressure buildup results from combustion of propane in air.

Peak deflagration pressure in closed equipment is approximately eight times the initial absolute pressure, whether atmospheric, subatmospheric, or elevated. This maximum pressure occurs at a concentration just slightly richer in fuel than the stoichiometric concentration for combustion in air (C_{st}), as shown in Table 26-14 for propane and methane:

Some flammable liquids generate a vapor pressure close to the C_{st} near normal room temperature, as shown in Table 26-15.

Toluene is a notoriously poor electrical conductor; even in grounded equipment it has caused several fires and explosions from static electricity. Near normal room temperature it has a concentration that is one of the easiest to ignite and, as previously discussed, that generates maximum explosion effects when ignited (Bodurtha, 1980, p. 39). Methyl alcohol has similar characteristics, but it is less prone to ignition by static electricity because it is a good conductor. Acetone is also a good conductor, but it has an equilibrium vapor pressure near normal room temperature, well above UFL. Thus, acetone is not flammable in these circumstances.

Several environmental factors affect maximum deflagration pressure and pressure rise, as highlighted in Table 26-16.

TABLE 26-14 Optimum Concentrations for Maximum Deflagration Pressure

	Stoichiometric concentration, vol %	Maximum deflagration pressure, vol %
Propane	4.0	5.0
Methane	9.5	10.3

TABLE 26-15 Liquids Having Equilibrium Vapor Pressure near the C_{st}

	Equilibrium vapor pressure at 20°C, vol %	C_{st}, vol %
Toluene	2.9	2.3
Methyl alcohol	12.6	12.2
Acetone (UFL = 12.8)	24.6	5.0

TABLE 26-16 Effect of Environmental Factors on Deflagration Pressure and Pressure Rise*

	Pressure	Temperature	Vessel volume	Turbulence	Strength of ignition
Maximum deflagration pressure	+	–	Minor	Minor	Minor
Maximum rate, deflagration pressure rise	+	+	–	+	+

*Unvented vessel: + = an increase in indicated factor increases pressure or pressure rise.
– = an increase in indicated factor decreases pressure or pressure rise.

Vessel volume has a large effect on the maximum rate of deflagration pressure rise; the cubic law states, all else being equal

$$(r_m)(V^{1/3}) = \text{constant } (K_G) \qquad (26\text{-}47)$$

where r_m = maximum rate of deflagration pressure rise, bar/s
V = volume, m^3
K_G = deflagration index for gases, bar·m/s

In compartmented equipment, higher deflagration pressure than noted in the preceding discussion can occur from pressure piling. After ignition in the first compartment, some of the gas mixture ahead of the flame front is pushed through a connection between the two compartments. Pressure of the original flammable mixture in the second compartment increases, and the resulting now-compressed mixture is ignited by the flame from the first compartment; abnormally high deflagration pressure may occur in this second compartment. This pressure piling effect is an important one and may pose difficult safety problems in design, if flammable mixtures cannot be prevented. As a rough guide, the ratio of compartment volumes of at least 5 to 1 apparently is required for pressure piling; generally, initial ignition must be in the larger compartment (Fitt, "Pressure Piling: A Problem for the Process Engineer," *Chem. Eng.* [Rugby, England], no. 368, pp. 237–239, May 1981.)

Detonation A deflagration can develop into a gaseous detonation in vessels and piping under certain conditions with enhanced explosion effects. Many factors affect detonation formation and effects. Briefly, upon ignition, pressure waves in a closed tube move through unburned gas. Subsequent waves move faster through the unburned gas, because of heating from previous pressure waves. Adiabatic compression results in high enough temperature to ignite gas ahead of the original flame and a detonation develops. (This ignition by compression to form a detonation is sometimes also called *pressure piling.*) The peak pressure in a stable detonation is on the order of 30 times the initial absolute pressure, disregarding the usually nondamaging spike of still higher pressure; reflected pressure is much higher than this 30 multiplier. (Special review is necessary for overpressure developed in an unstable [overdriven] detonation.) Nevertheless, in usual plant vessels without large length/diameter ratios, detonation is unlikely at 1 atm and near normal room temperature. Strong equipment may be subject to damage in a detonation, and rupture disks alone cannot control a detonation. Flame arresters are now commonly used to help protect against detonations; see the article on flame arresters in this section. But the best procedure to guard against the destructive effects of detonations is to prevent the formation of flammable mixtures.

Explosion Protection Where prevention of flammable mixtures may not be feasible, protection facilities must be installed; sometimes, too, backup explosion protection facilities are used in conjunction with inerting systems. Containment, suppression, or venting are used for protection against internal deflagrations in fuel-air mixtures. Although these methods may protect against deformation or rupture of a vessel, damage to internal appurtenances may still occur. Containment and suppression prevent the discharge of environmentally unacceptable materials to the atmosphere.

Containment The design pressure (maximum allowable working pressure) to prevent rupture of equipment for most gas-air mixtures initially at 1 atm should be 304 kPa gauge (44.1 psig), and to prevent permanent deformation, 608 kPa gauge (88.2 psig) (National Fire Protection Association, *Explosion Prevention Systems,* NFPA 69, Quincy, Mass., 1992, p. 11). NFPA 69 provides important additional design information on deflagration pressure containment.

Explosion Suppression With explosion suppression, an incipient explosion is detected and—within a few milliseconds—a suppressant is discharged into the exploding medium to stop combustion. Pressure and optical detection systems are used; suppressors are pressurized and release the suppressants when actuated by an electroexplosive device.

Deflagration pressure can be reduced substantially by suppression. Figure 26-30 shows the pressures measured in an ethylene-air explosion and a sodium bicarbonate-suppressed ethylene-air explosion. Fike Corporation, Blue Springs Missouri, and Fenwal Safety Systems, Marlborough, Mass., supply explosion suppression systems.

To reduce the chance of false activation of the suppression system by vibration, a flexible pressure detector standoff is often used. Also, two detectors in series may be employed to reduce further the possibility of false activation.

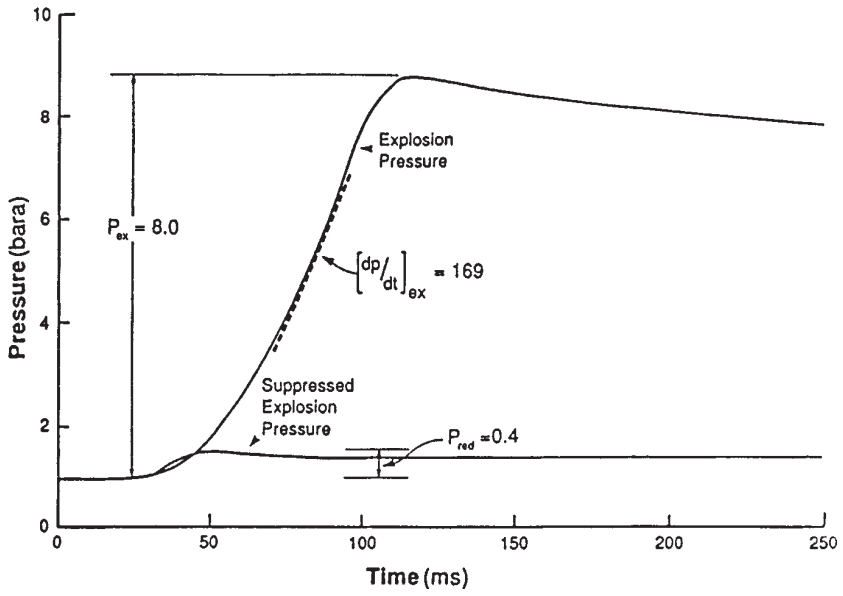


FIG. 26-30 Suppression of explosions. Pressures in an ethylene explosion and a sodium bicarbonate suppressed ethylene explosion. Tests conducted by Fike Corp. in a 1-m^3 vessel. Ethylene concentration = 1.2 times stoichiometric concentration for combustion. $(dp/dt)_{ex}$ = 169 bar/s (2451 psi/s). P_{red} = reduced explosion pressure = 0.4 bar gauge (5.8 psig). (*From Chatrathi, "Explosion Testing,"* Safety and Technology News, *vol. 3, issue 1, Fike Corp., 1989, by permission.*)

Explosion Venting The technology of explosion venting has advanced in recent years but is still not exact; thus, considerable care in sizing explosion vents is essential. The NFPA standard, *Guide for Venting of Deflagrations,* NFPA 68, provides excellent guidance on the practice of explosion venting.

Venting requirements in NFPA 68 are based on the cubic law in Eq. (26-47). The deflagration venting nomographs of the NFPA are subject to several caveats clearly specified in NFPA 68. Particularly, the nomographs do not apply with high initial turbulence. Moreover, the NFPA 68 nomographs must not be used for venting detonations, runaway reactions, or gas mixtures containing elevated oxygen compared to air.

Equations have been developed by L. L. Simpson for the Bartknecht nomographs for gases in NFPA 68 (Bartknecht, *Explosions,* Springer-Verlag, New York, 1981; Simpson, "Equations for the VDI and Bartknecht Nomograms," *Plant/Oper. Prog.,* vol. 5, no. 1, January 1986, pp. 49–51). Those equations are shown in Table 26-17 for quiescent methane, propane, and hydrogen. NFPA 68 explains how to determine vent areas for other gases and vapors. That determination is based on fundamental burning velocities. As an approximation without serious error, the equation for quiescent propane may be used, for example, for vent areas for the quiescent gases in Table 26-18.

The following precautions must be considered in application of the NFPA 68 nomographs or Simpson's equations:

1. Do not use relief valves as explosion vents.
2. Do not use rupture disks in series, unless the space between them is vented to air or a telltale is installed to warn of pressure buildup in that space.
3. Set the release pressure of a rupture disk or other vent closure as close to the operating pressure as practical. Note that the maximum overpressure in a vented explosion will exceed the opening pressure of the vent closure.
4. Locate explosion vents as close as possible to the most likely ignition sources.
5. Locate deflagration vents so discharge from them will not endanger personnel or damage equipment.
6. Install equipment to be vented outdoors, weather and other factors permitting.
7. Place equipment to be vented close to an exterior wall, if it must be placed indoors; the vent ducts should be free of bends and no longer than 3 m (10 ft).
8. *Do not discharge explosion vents within buildings;* serious fires and explosions have occurred by such venting.

TABLE 26-17 Explosion Venting Equation for Quiescent Gases

$$A_v = d \cdot V^f \cdot \exp(gP_{stat}) \cdot P_{red}^h$$

Gas	d	f	g	h
Methane	0.105	0.770	1.23	–0.823
Propane	0.148	0.703	0.942	–0.671
Hydrogen	0.279	0.608	0.755	–0.393

where d, f, g, h = constants as tabulated above
A_v = vent area, m^2
P_{red} = maximum explosion pressure during venting, bar g
P_{stat} = vent closure release pressure, bar g
V = vessel volume, m^3

TABLE 26-18 Vent Areas Calculated for Propane May Be Used for the Following Quiescent Gases

Acetone	Dimethyl ether
Acrylonitrile	Ethane
Benzene	Ethyl acetate
n-Butane	*n*-Heptane
Butanone	*n*-Hexane
1-Butene	Isopropyl alcohol
Carbon disulfide	*n*-Pentane
Cyclohexane	1-Pentene
Cyclopropane	Propylene
Diethyl ether	Toluene

9. Consider reaction forces on vented equipment from the discharge of explosion products from the vent.
10. Design the vents to prevent the development of damaging negative pressure from cooling of hot products of combustion.
11. Consider the safety of personnel in rooms or buildings if those spaces are to be vented, e.g., by vent panels.

UNCONFINED VAPOR CLOUD EXPLOSIONS (UVCEs) AND BOILING LIQUID EXPANDING VAPOR EXPLOSIONS (BLEVEs)

GENERAL REFERENCES: AIChE/CCPS, *Guidelines for Chemical Process Quantitative Risk Analysis,* New York, 1989. AIChE/CCPS, *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs,* New York, 1994. Bodurtha, *Industrial Explosion Prevention and Protection,* McGraw-Hill, New York, 1980. Brasie and Simpson, "Guidelines for Estimating Damage Explosion," *Chem. Eng., Prog. Second Loss Prev. Symp.,* St. Louis, 1968, pp. 91–102. Crowl and Louvar, *Chemical Process Safety: Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, N.J., 1990. Johansson, "The Disaster at San Juanico," *Fire J.,* vol. 80, no. 1, January 1986, pp. 32–37, 93–95. Kletz, "Protect Pressure Vessels from Fire," *Hydrocarbon Processing,* August 1977, pp. 98–102. Lees, *Loss Prevention in the Process Industries,* 2 vols., Butterworths, London, 1980. Martinsen, Johnson, and Terrell, "BLEVEs: Their causes, effects, and prevention," *Hydrocarbon Process.,* vol. 65, no. 11, November 1986, pp. 141, 142, 146, 148. Pietersen, "Analysis of the LPG Disaster in Mexico City," presented at the *Societe de Chemie Industrielle 5th Int. Symp. on Loss Prev. and Safety Promotion in the Process Ind.,* Cannes, 1986, vol. 1, preprints, pp. (21) 1–15. Pikaar, "Unconfined Vapour Cloud Dispersion and Combustion: An Overview of Theory and Experiments," *Chem. Eng. Res. Des.,* vol. 63, no. 2, March 1985, pp. 75–81. Prugh and Johnson, *Guidelines for Vapor Release Mitigation,* AIChE/CCPS, New York, 1988. Prugh, "Quantify BLEVE Hazards," *Chem. Eng. Prog.,* vol. 87, no. 2, February 1991, pp. 66–72. Prugh, "Quantitative Evaluation of Fireball Hazards," *Process Safety Prog.,* vol. 13, no. 2, April 1994, pp. 83–91. TNO, *Methods for the Calculation of the Physical Effects of the Escape of Dangerous Materials: Liquids and Gases ("The Yellow Book"),* Apeldoorn, The Netherlands, 1979. Walls, "Just What Is a BLEVE?," *Fire J.,* vol. 72, no. 6, November 1978, pp. 46–47.

See also General References in "Gas Dispersion" in this section.

Unconfined Vapor Cloud Explosions (UVCEs)

Background Unconfined vapor cloud explosions (also known as vapor cloud explosions) in open air often result when accidental releases of vapors or gases to the atmosphere are ignited. Astonishingly high pressure can result from an unconfined vapor cloud explosion; 70 kPa (10 psi) or so may occur at the outer edge of the exploding cloud, with still higher pressures near the center of the blast. Numerous severe explosions of this nature have occurred in past years (Lenoir and Davenport, "A Survey of Vapor Cloud Explosions: Second Update," *Process Safety Prog.,* vol. 12, no. 1, January 1993, pp. 12–33). In a survey of property damage losses in 100 large losses in the hydrocarbon-chemical industries, M & M Protection Consultants of Marsh & McLennan found that a vapor cloud was the initiating mechanism in 43 percent of the cases. Releases of liquefied dense gases have caused many of the reported UVCEs. Such heavy gases tend to hug the ground with limited dispersion in ambient air; this condition results in accumulation of these gases where they can cause maximum casualties to people and damage to property, if ignited. Notwithstanding, releases of mammoth amounts of *compressed* natural gas from ruptured pipelines have caused vapor cloud explosions. As an example, in 1969 a 356-mm (14-in) pipeline carrying natural gas at more than 5378 kPa gauge (780 psig) ruptured; about 8 to 10 min later the escaping gas exploded violently (National Transportation Safety Board, *Pipeline Accident Report Mobil Oil Corporation, High-Pressure Natural Gas Pipeline Accident, Houston, Texas, September 9, 1969,* NTBS-Par-71-1, Washington, D.C., 1971).

Elevated emergency unflared releases with vents of sufficient height normally do not cause damaging overpressure at the ground, if accidentally ignited (Bodurtha, "Vent Heights for Emergency Releases of Heavy Gases," *Plant/Operations Prog.,* vol. 7, no. 2, April 1988, pp. 122–126).

Numerous tests on dispersion of heavy gases and on causes of UVCEs have been performed in recent years. Dispersion tests and computer models based on them may not be representative of all

conditions at a plant, however, because of equipment plus heat sources that cause better spreading of a plume than is modeled in tests.

Moreover, vapors flashed from release of a liquefied gas will be cold; such vapors flowing over warmer ground may promote atmospheric instability with accompanying turbulence and, thereby, cause more mixing with ambient air than in some tests. In addition, some tests have been so-called meteorological area sources, while the dispersion equations are generally meteorological point sources. (Only concentrations relatively close to the location of discharge of the vapors will be affected by this difference in sources.) Also, the *momentary* concentration of a combustible gas or flammable vapor is the important duration of a concentration for UVCEs; not all dispersion models specify their averaging time of concentrations. Thus, *predictions of concentrations must be treated as estimates.*

Dispersion One way to determine concentrations is with a modified gaussian dispersion equation (Bodurtha, 1980). (See "Gas Dispersion" in this section for discussion of and references to other methods plus definition of atmospheric stabilities.) In that equation, *E* atmospheric stability is used for dense gases for all light to moderate wind speeds, whatever the actual atmospheric stability may be. The equation in Bodurtha (1980) overpredicts concentrations close to an emission source for a dense gas where the major effects of a UVCE are experienced, and, therefore, where uncertainty exists, is on the safe side. On the other hand, the modified gaussian equation underpredicts concentrations for dense gases at relatively large distances, and it should not be used for such gases beyond about 1000 m. Concentrations determined from the equation in Bodurtha (1980) are compared in Table 26-19 with concentrations of ammonia (which was dense by virtue of coldness) in Desert Tortoise Series Test #4 (Goldwire, "Large-Scale Ammonia Spill Tests," *Chem. Eng. Prog.,* vol. 82, no. 4, April 1986, pp. 35–41); wind speed is 4.5 m/s (10 mi/h); and vapor release rate for calculated values in the table is 108.8 m^3/s. (Calculated momentary concentrations include a *virtual source,* i.e., a fictitious upwind source so that concentrations equal 100 percent—and no more—at the release point.)

In assessing the hazard of a UVCE or in investigating a UVCE it is often necessary to (1) estimate the maximum distance to the lower flammable limit (LFL) and (2) determine the amount of gas in a vapor cloud above the LFL. Figure 26-31 shows the maximum distance to the lower flammable limit, i.e., in the centerline of the cloud, based on the previous method from Bodurtha (1980) for wind speeds of 1 m/s (2.2 mi/h) and 5 m/s (11 mi/h). Maximum concentrations probably occur near 1 m/s. The volume of fuel from the LFL up to 100 percent may be estimated by

$$V_f = 0.64 \cdot Q \cdot x_L/u \qquad (26\text{-}48)$$

where V_f = volume of fuel (no air) from the LFL up to 100%, m^3 at 25°C
Q = continuous dense vapor emission rate, m^3/s at 25°C
x_L = distance to momentary LFL in centerline of cloud, m
u = wind speed, m/s

For application of Eq. (26-48), x_L should not exceed 300 m (984 ft). The reason for selecting 100 percent, instead of the upper flammable limit (UFL), in the equation for V_f is that in an incipient explosion vapor above the UFL may be mixed with additional air and, thereby, contribute to explosion pressure.

TABLE 26-19 Comparison of Measured and Calculated Ammonia Concentrations in Ammonia Spill Tests

Distance from release, m	Measured concentrations by Goldwire, vol %	Calculated momentary concentrations,* vol %
200	4.9	11.6
300	4.0	7.2
500	3.0	3.6
800	2.1	1.8
1000	1.7	1.3

*From equation in Bodurtha, 1980.

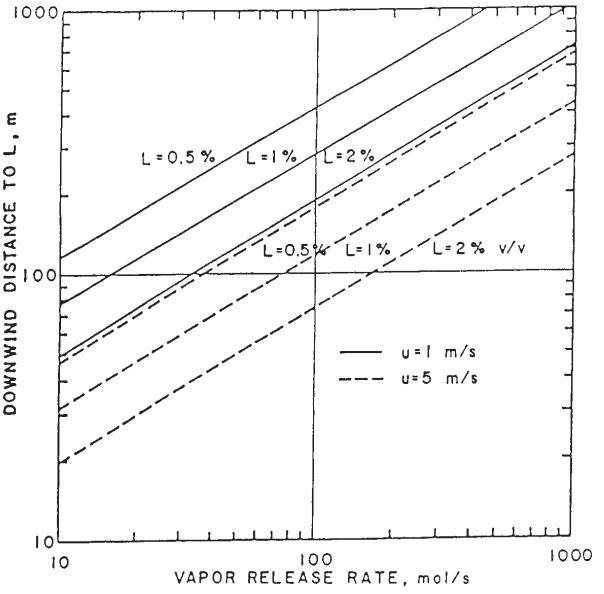


FIG. 26-31 Estimated maximum downwind distance to lower flammable limit *L,* percent by volume at ground level in centerline of vapor cloud, vs. continuous dense vapor release rate at ground level. *E* atmospheric stability. Level terrain. Momentary concentrations for *L.* Moles are gram moles; *u* is wind speed. (*From Bodurtha, 1980, p. 105, by permission.*)

Pressure Development Overpressure in a UVCE results from turbulence that promotes a sudden release of energy. Tests in the open without obstacles or confining structures do not produce damaging overpressure. Nevertheless, combustion in a vapor cloud within a partially confined space or around turbulence-producing obstacles may generate damaging overpressure. Also, turbulence in a jet release, such as may occur with compressed natural gas discharged from a ruptured pipeline, may result in blast pressure.

Example The combustion process in large vapor clouds is not known completely and studies are in progress to improve understanding of this important subject. Special study is usually needed to assess the hazard of a large vapor release or to investigate a UVCE. The TNT equivalent method is used in this example; other methods have been proposed. Whatever the method used for dispersion and pressure development, a check should be made to determine if any governmental unit requires a specific type of analysis.

Assume a continuous release of pressurized, liquefied cyclohexane with a vapor emission rate of 130 g mol/s, 3.18 m^3/s at 25°C (86,644 lb/h). (See "Discharge Rates from Punctured Lines and Vessels" in this section for release rates of vapor.) The LFL of cyclohexane is 1.3 percent by vol., and so the maximum distance to the LFL for a wind speed of 1 m/s (2.2 mi/h) is 260 m (853 ft), from Fig. 26-31. Thus, from Eq. (26-48), $V_f \approx 529\ m^3 \approx 1817$ kg. The volume of fuel from the LFL up to 100 percent at the moment of ignition for a continuous emission is *not* equal to the total quantity of vapor released; that V_f *volume stays the same even if the emission lasts for an extended period* with the same values of meteorological variables, e.g., wind speed. For instance, in this case 9825 kg (21,661 lb) will have been emitted during a 15-min period, which is considerably more than the 1817 kg (4005 lb) of cyclohexane in the vapor cloud above LFL. (A different approach is required for an instantaneous release, i.e., when a vapor cloud is explosively dispersed.) The equivalent weight of TNT may be estimated by

$$W_{TNT} = \frac{0.01 \cdot \alpha \cdot H_c \cdot W_c}{4.52} \qquad (26\text{-}49)$$

where W_{TNT} = equivalent weight of TNT, kg
α = explosion efficiency of UVCE, %

H_c = lower heat of combustion of flammable vapor, MJ/kg
W_c = weight of flammable vapor between LFL and 100% for continuous release, kg

and energy of detonation of TNT = 4.52 in MJ/kg.

The explosion efficiency α is difficult to assess; it appears that the maximum efficiency for vapor between the LFL and 100 percent, as in this example, is 10 to 20 percent. So, for this case with $\alpha = 10$ percent, H_c for cyclohexane = 43.84 MJ/kg, and $W_c = 1817$ kg, the $W_{TNT} = 1762$ kg. Thus, 1 kg of cyclohexane, or generally any hydrocarbon at 10 percent explosion efficiency, equals 1 kg TNT. Overpressure may be estimated from "Guidelines for Estimating Damage" in this section. (See "Guidelines for Estimating Damage Explosion" by Brasie and Simpson and "Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs," New York, 1994, in General References for other procedures.)

Prevention and Protection It is difficult to cope with a potential UVCE once an accidental release has occurred. Consequently, *the best procedure to guard against a UVCE is to prevent the release in the first place.* Safe piping is essential to protect against UVCEs. Forty percent of all major plant losses are due to piping failures, and corrosion is one of the largest single causes of plant and equipment breakdown (Hancock, "Safer Piping: Awareness Training for the Process Industries," *Plant/Oper. Prog.*, vol. 9, no. 2, April 1990, pp. 114–116). Moreover, mistakenly open valves that caused mammoth emissions of hydrocarbons have resulted in two major UVCEs with a total of 29 deaths in those two instances. Thus, close scrutiny regarding piping and valves is mandatory to help prevent UVCEs. Some other protection methods are summarized as follows.

Remotely Operated Shutoff Valves These should be considered for supply lines and other vulnerable pipelines. Excess flow valves that close when flow exceeds a set amount are possible substitutes, but they are not acceptable to some operators.

Flammable Vapor Detectors These should be installed to warn of leaks, although such devices do not effectively control UVCEs with sudden, massive releases.

Elevated or Remote Air Intakes Elevated or remote air intakes for control rooms will help in reducing ingress of dense, flammable vapors into those rooms. Ordinarily, elevating the tip of the air intake duct 9 m (30 ft) above the ground is sufficient. Installing flammable vapor detectors in the air intake ducts provides additional protection. Controls that automatically stop air to control rooms if vapor concentrations reach 25 percent of their LFL should also be considered.

Intentional Ignition Intentional ignition to ignite a vapor cloud early before it spreads out to a large volume has been used or considered only rarely. Such ignition should not be employed for control of UVCEs solely without thorough study of the ramifications of its use. (In some infrequent cases when the gas is both flammable and particularly toxic, intentional ignition may be warranted.)

Large Fans These could be used to dilute a vapor cloud below its LFL with ambient air (see, for example, Whiting and Shaffer, "Feasibility Study of Hazardous Vapor Amelioration Techniques," *Proc. 1978 Nat. Conf. on Control of Hazardous Material Spills,* USEPA, Miami Beach, April 1978). But caution must be exercised because the turbulence produced by fans will likely promote rapid combustion and a resulting UVCE unless vapors are diluted below the LFL. Nevertheless, in new plants, strategic placement of air coolers may provide enough air flow to reduce the risk of a UVCE.

Water Sprays and Steam Curtains These have been used and/or advocated to help protect against a UVCE. Such devices entrain air to dilute a vapor cloud. Also, some claim that water curtains form a physical barrier to stop the flow of the vapor cloud. As with large fans, vapors need to be reduced below LFLs to decrease the possibility of UVCEs from enhanced turbulence by the sprays or curtains. Moodie studied water spray barriers using carbon dioxide to approximate a heavy, flammable vapor cloud (Moodie, "The Use of Water Spray Barriers to Disperse Spills of Heavy Gases," *Plant/Oper. Prog.*, vol. 4, no. 4, October 1985, pp. 234–241). He used CO_2 rates of 2 and 4.2 kg/s (15,859 and 33,304 lb/h). (Propane would give the same vapor rates as these CO_2 weight rates.) There may be an upper practical limit for the emission rate of heavy gases that can be effectively dispersed by water sprays or steam curtains (Seifert, Maurer, and Giesbrecht, "Steam Curtains—Effectiveness and Electrostatic Hazards," presented at the *Institution of Chemical Engineers 4th Int. Symp. on Loss Prevention and Safety Promotion in the Process Ind.,* Harrogate, England, 1983, vol. 1, preprints, pp. F1–F12). In any event, this equipment could be useful near known ignition sources, such as furnaces, to guard against a UVCE. Steam will be electrically charged with steam curtains. Care must be taken to assure that nearby electrical conductors are grounded. If not, the conductor could obtain an electrostatic charge from the steam and cause an incendiary spark for ignition of the vapor cloud.

Release of a pressurized, liquefied gas to the atmosphere will cause the gas to cool and condense water vapor in ambient air, forming a visible vapor cloud. Firefighters and operators who attempt to move such a cloud away from furnaces and the like with fire hoses and water jet guns are at risk, because of the possibility of a UVCE near them. Plants and governmental agencies who recommend such practices need to reexamine their policies.

Structures Structures that include partially confined spaces and turbulence-producing obstacles such as pipe bridges plus closely packed equipment, promote UVCEs. This undesirable architecture—relative to UVCEs—is often a product of congestion on a plant. Congestion is an enemy of safety. Thus, the probability of a UVCE, plus property losses and casualties, will likely be greater at a congested plant than at an uncongested site.

Vapor cloud explosions also occur indoors when large amounts of flammable vapors are discharged accidentally into buildings. Turbulence from the myriad of equipment and piping in an operating building likely cause a sudden release of energy for the room-air explosion. As one of several examples, seven were killed when vinyl chloride exploded in a building after failure of a sight glass (Walls, "Vinyl Chloride Explosion," *Natl. Fire Prot. Assoc. Q.,* vol. 57, no. 4, April 1964, pp. 352–362).

Strong Buildings Strong buildings may be prudent where people congregate, such as control rooms. For new plants, serious consideration must be given to stronger design of buildings that are vulnerable to a UVCE, compared to past designs.

BLEVEs can occur when a vessel containing a liquid above its atmospheric boiling point ruptures. The resulting ultrarapid vaporization of much of the liquid results in fire, if the liquid is flammable, plus overpressure. (Initial catastrophic failure of the vessel must occur for a BLEVE; the opening of a relief valve does not cause a BLEVE, nor does it necessarily protect against one.) BLEVE overpressure has occurred with pressurized *nonflammable* liquids, such as chlorine and carbon dioxide (Clayton and Griffin, "Catastrophic Failure of a Liquid Carbon Dioxide Storage Vessel," *Process Safety Prog.,* vol. 13, no. 4, October 1994, pp. 202–209).

Cause As discussed by Prugh (1991) and others, BLEVES can occur from:

1. Mechanical damage caused, for example, by corrosion or collision
2. Overfilling and no relief valve
3. Runaway reaction or polymerization—e.g., vinyl chloride monomer (Kim-E and Reid, "The Rapid Depressurization of Hot, High Pressure Liquids or Supercritical Fluids," chap. 3, in M. E. Paulaitis et al., eds., *Chemical Engineering at Supercritical Fluid Conditions,* Ann Arbor Science, 1983, pp. 81–100)
4. Overheating with an inoperative relief valve
5. Vapor-space explosion
6. Mechanical failure
7. Exposure to fire

A common cause of a BLEVE in plants of the hydrocarbon-chemical industry is exposure to fire. With an external fire below the liquid level in a vessel, the heat of vaporization provides a heat sink, as with a teakettle; evolved vapors exit through the relief valve. But if the flame impinges on the vessel above the liquid level, the metal will weaken and may cause the vessel to rupture suddenly, even with the relief valve open. The explosive energy for a BLEVE comes from superheat. This energy is at a maximum at the superheat limit temperature. (SLT is the maximum temperature to which a liquid can be heated before homogeneous nucleation occurs with explosive vaporization of the liquid and accompanying overpressure.) The SLT

depends on the final pressure attained, and with letdown to 1 atm, it may be estimated by the simple relationship (Porteous and Reid, "Light Hydrocarbon Vapor Explosions," *Chem. Eng. Prog.,* vol. 72, May 1976, pp. 83–89):

$$\text{SLT} = 0.89\ T_c \tag{26-50}$$

where T_c is the critical absolute temperature. With propane, for example, SLT from Eq. (26-50) = 57°C, only a degree or so higher than the measured value (Reid, in *Advances in Chemical Engineering,* vol. 12, Academic Press, New York, 1983).

Fireballs Giant hazardous fireballs result from large BLEVEs. Several formulas for BLEVE physical parameters and thermal radiation hazards have been summarized by the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers and by Prugh. (See AIChE/CCPS, 1989; Prugh, 1994.) For the maximum fireball diameter, D_{max} in meters, CCPS has selected

$$D_{max} = 6.48\ M^{0.325} \tag{26-51}$$

where M is the initial weight of the flammable liquid, in kilograms. Thus, the maximum diameter of a propane fireball from an initial propane weight of 150 metric tons (150,000 kg = 330,690 lb) is 312 m (1024 ft).

Overpressure Significant blast overpressures result from BLEVEs. In addition, portions of ruptured tanks may rocket large distances with clear danger to firefighters and innocent onlookers. In one test it was reported that the BLEVE blast overpressure before ignition about 10 m (33 ft) away from an exploding tank initially containing 450 kg (992 lb) propylene was 75 kPa gauge (10.9 psi). Assuming that pressure to be incident (side-on) blast pressure, it can be determined from Fig. 26-9 that W_{TNT} = 23.3 kg (51.4 lb), i.e., about 5 percent of the initial weight of propylene.

Prevention and Protection Several methods may be used to protect against the causes of BLEVEs itemized earlier in this part of Section 26. They include thermal insulation, water cooling, depressuring facilities, corrosion control, and ground sloping (see Kletz, 1977; Martinsen et al., 1986; Prugh, 1991). A desirable diking method with ground sloping to minimize impingement of flame on a tank is shown in Fig. 26-32.

Fauske has suggested two passive designs for prevention of BLEVEs (Fauske, "Preventing Explosions During Chemicals and Materials Storage," *Plant/Oper. Prog.* vol. 8, no. 4, October 1989, pp. 181–184). One method keeps a normally unwetted internal surface of a tank wet; the second surrounds the high-pressure storage tank with an open atmospheric tank filled with water. Additional BLEVE prevention and protection methods follow.

1. *Minimize inventory* to the extent feasible. Expected benefits from minimum inventory may be offset by hazards resulting from more frequent and smaller shipments. The relative hazards should be reviewed (Englund, "Design and Operate Plants for Inherent Safety—Part 1," *Chem. Eng. Prog.,* vol. 87, no. 2, March 1991, pp. 85–91).
2. *Consider refrigerated storage* at atmospheric pressure. A BLEVE cannot occur with the liquid at its atmospheric boiling point (no superheat), although a fire hazard may still exist. The Dow Chemical Company in Texas stores chlorine as a liquid at atmospheric pressure at about –34°C (Englund, ibid. 1991).
3. *Set the safety relief valve* to open as far below the pressure corresponding to the SLT at 1 atm as is feasible (Reid, "Possible Mechanism for Pressurized-Liquid Tank Explosions or BLEVE's," *Science,* vol. 23, March 23, 1979, pp. 1263–1265). The pressure at propane's SLT of 57°C is 2000 kPa abs. (290 psia = 275 psig).
4. *Eliminate turned-down vents* from safety relief valves, i.e., upside down U. Possible accidental ignition of releases from such vents will likely result in flame impingement on the top external surface of the tank, above the internal wetted surface. BLEVE! Some means to handle rainwater from a desirable upward vertical vent have been listed by Bodurtha (ibid., April 1988). Moreover, a safety relief valve must function properly when required and must be sized properly to help prevent an explosion.

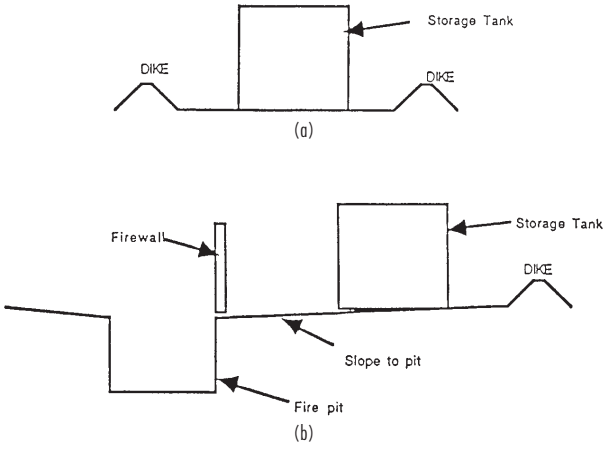


FIG. 26-32 Methods of diking for flammable liquids: (*a*) traditional diking method allows leaks to accumulate around the tank. In case of fire, the tank will be exposed to flames that can be supplied by fuel from the tank and will be hard to control. (*b*) In the more desirable method, leaks are directed away from the tank. In case of fire, the tank will be shielded from most flames and fire will be easier to fight. (*From Englund, in* Advances in Chemical Engineering, *vol. 15, Academic Press, San Diego, 1990, pp. 73–135, by permission.*)

DUST EXPLOSIONS

GENERAL REFERENCES: Bartknecht, *Dust Explosions,* Springer, New York, 1989. Bartknecht, *Explosionsschutz* (Explosion Protection), Springer, Berlin, 1993. Crowl/Louvar, *Chemical Process Safety,* Prentice Hall, New Jersey, 1990. "Dust Explosions," *28th Annual Loss Prevention Symposium,* Atlanta, Georgia, 1994. Eckhoff, *Dust Explosions in the Process Industries,* Butterworth-Heinemann, London 1991. *Health, Safety and Loss Prevention in the Oil, Chemical and Process Industries,* Butterworth-Heinemann, Singapore, 1993. NFPA 69, *Standard on Explosion Prevention Systems,* 1992. VDI-Report 975, *Safe Handling of Combustible Dust,* VDI-Verlag GmbH, Düsseldorf, 1992. VDI-Guideline 2263, *Dust Fires and Dust Explosions,* Beuth Verlag, Berlin, 1992.

Definition of Dust Explosion A dust explosion is the rapid combustion of a dust cloud. In a confined or nearly confined space, the explosion is characterized by relatively rapid development of pressure with a flame propagation and the evolution of large quantities of heat and reaction products. The required oxygen for this combustion is mostly supplied by the combustion air. The condition necessary for a dust explosion is a simultaneous presence of a dust cloud of proper concentration in air that will support combustion and a suitable ignition source.

Explosions are either deflagrations or detonations. The difference depends on the speed of the shock wave emanating from the explosion. If the pressure wave moves at a speed less than or equal to the speed of sound in the unreacted medium, it is a *deflagration;* if it moves faster than the speed of sound, the explosion is a *detonation.*

The term *dust* is used if the maximum particle size of the solids mixture is below 500 μm.

In the following, only dusts are called combustible in the airborne state if they require oxygen from the air for exothermic reaction.

Glossary

***activation overpressure*, P_a** That pressure threshold, above the pressure at ignition of the reactants, at which a firing signal is applied to the suppressor(s).

cubic low The correlation of the vessel volume with the maximum rate of pressure rise. $V^{1/3} \cdot (dP/dt)_{max} = \text{constant} = K_{max}$

dust Solid mixture with a maximum particle size of 500 μm.

dust explosion class, St Dusts are classified in accordance with the K_{max} values.

equivalent ignition energy (EIE) The amount of energy which, when transformed into an electrical spark discharge, has the same incendivity as the ignition source under characterization.

explosion Propagation of a flame in a premixture of combustible gases, suspended dust(s), combustible vapor(s), mist(s), or mixtures thereof, in a gaseous oxidant such as air, in a closed, or substantially closed, vessel.

explosion pressure resistant (EPR) Design of a construction following the calculation and construction directions for pressure vessels.

explosion pressure-shock resistant (EPSR) Design of a construction allowing greater utilization of the material strength than the EPR design.

limiting oxygen concentration (LOC) Maximum oxygen concentration in a mixture of a combustible and air and inert gas, in which an explosion will not occur.

***maximum explosion overpressure*, P_{max}** The maximum pressure reached during an explosion in a closed vessel through systematically changing the concentration of dust-air mixture.

***maximum reduced explosion overpressure*, $P_{red,max}$** The maximum pressure generated by an explosion of a dust-air mixture in a vented or suppressed vessel under systematically varied dust concentrations.

***maximum explosion constant*, K_{max}** Dust and test-specific characteristic calculated from the cubic law. It is equivalent to the maximum rate of pressure rise in a 1-m^3 vessel.

***maximum rate of pressure rise*, $(dP/dt)_{max}$** The maximum rate of pressure rise obtained in a closed vessel through systematically changing the concentrations of a dust-air mixture.

minimum ignition energy (MIE) Lowest electrical energy stored in a capacitor which, upon discharge, is just sufficient to effect ignition of the most ignitable atmosphere under specified test conditions.

minimum ignition temperature (MIT) The lowest temperature of a hot surface on which the most ignitable mixture of the dust with air is ignited under specified test conditions.

***static activation overpressure*, P_{stat}** Pressure which activates a rupture disk or an explosion door.

***vent area*, A** Area of an opening for explosion venting.

venting capability, EF Measure to evaluate the efficiency of the pressure relief device in comparison with a rupture disk with the same vent area.

Prevention and Protection Concept against Dust Explosions Explosion protection encompasses the measures implemented against explosion hazards in the handling of combustible substances and the assessment of the effectiveness of protective measures for the avoidance or dependable reduction of these hazards. The explosion protection concept is valid for all mixtures of combustible substances and distinguishes between:

1. Measures which prevent or restrict formation of a hazardous, explosible atmosphere
2. Measures which prevent the ignition of a hazardous, explosible atmosphere
3. Constructional measures which limit the effects of an explosion to a harmless level

From a safety standpoint, priority must be given to the measures in item 1. Group 2 cannot be used as a sole protective measure for flammable gas or solvent vapors in industrial practice with sufficient reliability, but can be applied as the sole protective measure when only combustible dusts are present if the minimum ignition energy of the dusts is high (>10 mJ) and the operating areas concerned can easily be monitored.

If the measures under (1) and (2), which are also known as *preventive measures,* cannot be used with sufficient reliability, the *constructional measures* (3) must be applied.

Preventive Explosion Protection The principle of preventive explosion protection comprises the reliable exclusion of one of the requirements necessary for the development of an explosion. In pictorial terms, therefore, at least one of the sides of the hazard triangle shown in Figure 26-33 will be broken open.

An explosion can thus be excluded with certainty by:

- Avoiding the development of explosible mixtures
- Replacing the atmospheric oxygen by *inert gas,* working in a vacuum, or using *inert dust*
- Preventing the occurrence of effective ignition sources

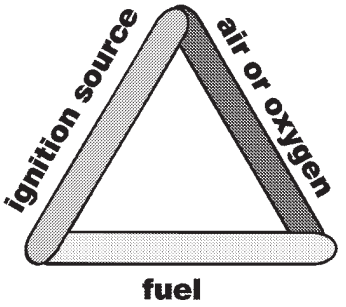


FIG. 26-33 Hazard triangle: principle of preventive explosion protection.

Avoidance of Explosible Combustible Substance-Air Mixtures For combustible dusts, the explosibility limits do not have the same meaning as with flammable gases and flammable vapors, owing to the interaction between dust layers and suspended dust. This protective measure can, for example, be used when dust deposits are avoided in operating areas or in the air stream of clean air lines after filter installations where in normal operation the lower explosibility limit is not reached. However, dust deposits must be anticipated with time. When these dust deposits are whirled up in the air, an explosion hazard can arise. Such a hazard can be avoided by regular cleaning. The dust can be extracted directly at its point of origin by suitable ventilation measures.

Avoidance of Explosions through Inerting The introduction of inert gas in the area to be protected against explosions lowers the oxygen volume content below the limiting oxygen concentration (LOC) so that ignition of the mixture can no longer take place. This process is called *inerting.*

One has to be aware of the danger of asphyxiation from gases in inerted equipment. This is also important for surrounding areas in case of major leaks.

Inerting is *not* a protective measure to avoid exothermic decompositions. For the avoidance of (smoldering) fires, oxygen concentrations lower than the LOC must usually be adhered to and must be determined from case to case. In addition to the nitrogen normally used, all nonflammable gases which do not support combustion or react with the combustible dust can be considered for use as the inert gas. The inerting effect generally decreases in the following order: carbon dioxide → water vapor → flue gas → nitrogen → noble gases. In special gases, liquid nitrogen or dry ice is used.

The LOC depends upon the combustible material and the type of inert gas used. It decreases with increased temperature and pressure. A distinction has to be made between the determined LOC value and the concentration which results by subtracting a safety margin.

The maximum allowable oxygen concentration (MAOC), which is, in general, 2 vol % below the LOC, has to include the following considerations: fluctuation in oxygen concentrations due to process and breakdown conditions per time and location, as well as the requirement for protective measures or emergency measures to become effective. In addition, a concentration level for an alarm has to be set below the MAOC.

For example, in rotary vacuum dryers it is possible to prevent the formation of explosible dust-air mixtures by setting and monitoring a certain partial vacuum (negative pressure). This pressure value must be determined by experiment for each type of dust. With pressures of less than 0.1 bar, in general, hazardous effects of dust explosions need not be anticipated. If the vacuum system malfunctions, the partial vacuum must be released by inert gas and the installation shut down.

Explosible dusts can also be changed into mixtures which are no longer explosible by the addition of inert dusts (e.g., rock salt, sodium sulfate). In general, inert dust additions of more than 50 wt % are necessary here. It is also possible to replace flammable solvents and cleaning agents by nonflammable halogenated hydrocarbons or water, or flammable pressure transmission fluids by halocarbon oils.

Avoidance of Effective Ignition Sources Explosions can be prevented if ignition sources capable of igniting combustible material-air mixtures can successfully be avoided. A distinction is made between *trivial ignition sources* (e.g., welding, smoking, cutting) and *ignition sources expected if operational malfunctions occur* (e.g., mechanically generated sparks, mechanically generated hot surfaces, lumps of smoldering material, static electricity). Trivial ignition sources can also reliably be excluded by organizational measures such as the systematic employment of permits.

For every installation, a check has to be made to determine which ignition source may become effective and whether it can be prevented with a sufficient degree of safety. With more sensitive products and complex installations, it becomes more and more difficult to exclude ignition sources with ample safety (Siwek et al., "Ignition Behavior of Dusts," *Proc. Loss Prevention Symposium,* Atlanta, April 12–19, 1994).

Mechanically generated sparks and *resultant hot surfaces* together are regarded as one of the more important causes of ignition in industrial practice. With mechanically generated sparks, a distinction is made between grinding, impact, and friction sparks which are formed by brief contact (<5 s) between materials. Mechanically generated hot surfaces, on the other hand, are formed by relatively long rubbing (>>5 s) against steel. The hot surfaces show considerably better incendivity in comparison with the short-lived mechanically generated sparks. Neither ignition source appears in industrial practice from the normal metallic materials of construction rubbing against each other or against stone if the relative circumferential speeds v_c are less than or equal to 1 $m \cdot s^{-1}$ (see Table 26-20). This is not valid for cerium-iron, titanium, and zirconium.

TABLE 26-20 Influence of Relative Circumferential Speeds v_c on Danger of Ignition for Combustible Dusts

$v_c \le 1$ $m \cdot s^{-1}$	There is no danger for ignition.
$v_c > 1$ .. 10 $m \cdot s^{-1}$	Every case has to be judged separately, considering the product and material-specific characteristics.
$v_c > 10$ $m \cdot s^{-1}$	In every case there is danger for ignition.

The ignition behavior of mechanically generated sparks in dust-air mixtures depends on the *minimum ignition energy* (MIE) and the *minimum ignition temperature* (MIT) of the dust in question. The ignition effectiveness of mechanically generated sparks decreases from *steel-friction sparks* to *steel-grinding sparks* to *aluminum/rust-impact sparks.* According to Fig. 26-34, it can be stated that the type of spark-producing material, together with the MIT and the MIE requirement, determines whether an ignition of dust-air mixture has to be anticipated from friction, grinding, or impact sparks. The mechanically generated sparks can thus be assigned different equivalent ignition energies toward dust-air mixtures with an MIT of less than or equal to 500°C. For example, if the MIT of a dust is 300°C, steel-friction sparks can ignite this dust only with an MIE (equivalent energy) up to 3000 mJ. The equivalent energy, also known as the *equivalent ignition energy* (EIE), is the amount of energy which, when transformed into an electrical spark discharge, has the same incendivity as the sparks shown in Fig. 26-34.

Mechanically generated hot surfaces represent an ignition hazard if, irrespective of the MIT and the MIE, the *surface temperature* is 1100°C or higher and the *hot surface area* by itself is large enough (see Fig. 26-35). Higher surface temperatures and larger surfaces have a better incendivity; lower temperatures and smaller surfaces have a poorer incendivity.

Lumps of smoldering material always represent a hazard when the dust can be classed as capable of forming such lumps; i.e., its burning behavior class at 100°C is greater than 3. A smoldering lump surface of a cube, A_o = 9600 mm^2, and a surface temperature, T_o = 900°C, is sufficient to ignite the mixtures of dusts with an MIT of less than 600°C (see Fig. 26-35). Higher surface temperatures and larger surfaces have a better incendivity; lower temperatures and smaller surfaces, a poorer incendivity.

An *electrostatic ignition source* (see also material on static electricity) which follows an electrostatic discharge can be incendive when the energy released is equal to or greater than the minimum ignition energy of a mixture. The energy released depends, among other things, on the type of discharge. This in turn depends on the geometry and material of the participating surfaces as well as on certain other conditions. The following overview summarizes the ignition behavior of several types of electrostatic discharges (see Table 26-21).

The experimental investigations of numerous dusts with different ignition sources have shown that the incendivity of an ignition source is not only influenced by its energy content, but the nature of the source also plays a role (Glor et al., "Recent Developments in the Assessment of Electrostatic Hazards Associated with Powder Handling," *Proc. 8th Int. Symposium Loss Prevention and Safety Promotion in the Process Industries,* Antwerp, Elsevier, Amsterdam, 1995). The minimum ignition energy determined by the standard procedure can also be used for the assessment of the incendivity of such ignition sources.

Brush Discharge With dusts with MIE values of less than 3 mJ determined with purely capacitive spark discharges (without induc-

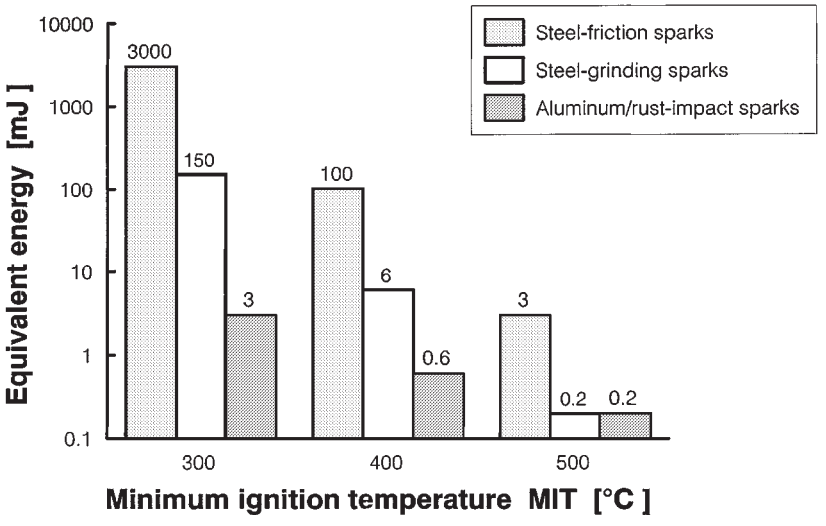


FIG. 26-34 Equivalent energies of mechanically generated sparks.

TABLE 26-21 Examples of Different Types of Electrostatic Discharges

Ignition sources	Requirement for formation	Incendivity for
Brush discharge	A nonuniform electric field between a charged dielectric and a conductor that has a moderate radius of curvature	MIE < 3 mJ
Bulk surface discharge	In rapid heaping of highly insulated bulk material, particularly when coarse material (diameter ≥ 1 mm) is present	MIE < 1 J (silo diameter 3 m)
Spark discharge	Ungrounded, conductive object	MIE < 1 J
Propagating brush discharge	Very high charging of nonconductive material, preferably in contact with a conductive surface	MIE < 10 J

tance), an ignition by brush discharges cannot be excluded with certainty. With such *extremely easily ignitable* dusts, the use of the protective measure, "avoidance of effective ignition sources," by itself is generally not sufficient. In this case, the brush discharge must also be considered as an ignition source, although it is normally important only for gases and vapors. For such dusts, the protective measure, "inerting" or "constructional explosion protection," must be used during large-scale handling operations. Toward dust-air mixtures, the brush discharges are assigned an equivalent ignition energy EIE ≤ 3 mJ for safety considerations.

Bulk Surfaces Discharge (Conical Pile Discharge) These discharges may also be generated with fine powder and not just with granules, as was previously assumed. These discharges from fine powder have, however, a much less equivalent ignition energy EIE compared to those associated with granules. The energy of conical pile discharges increases with increasing silo diameter. The probability of their occurrence increases with increasing charge-to-mass ratio in the powder and increasing mass filling rate. Findings to date show that the EIE of conical pile discharges using highly insulating granules for generating the discharges toward dust-air mixtures is about 1 J if the silo diameter is restricted to 3 m. Because of the large diameters, the granules generating the discharges are unlikely to give dust explosions; therefore, a possible explosion hazard must be associated with the simultaneous presence of an explosible cloud of an additional, fine dust fraction. This may be the explanation for why the frequency of the occurrence of an explosion in silos initiated by bulk surfaces discharges is relatively low.

Sparks Discharge Spark discharges can ignite dust-air mixtures up to an MIE of 1 J. If an uncertainty area is taken into account, this corresponds to an EIE of 1 to 10 J.

Propagating Brush Discharge The incendivity of the propagating brush discharge is so large that an ignition of dust-air mixtures with an MIE up to around 100 J must be anticipated. For dust-air mixtures, this corresponds to an EIE range of 10 to 100 J.

For industrial practice, the following principles have resulted for the protective measures to be implemented. Their application is selective and depends on the prevailing circumstances.

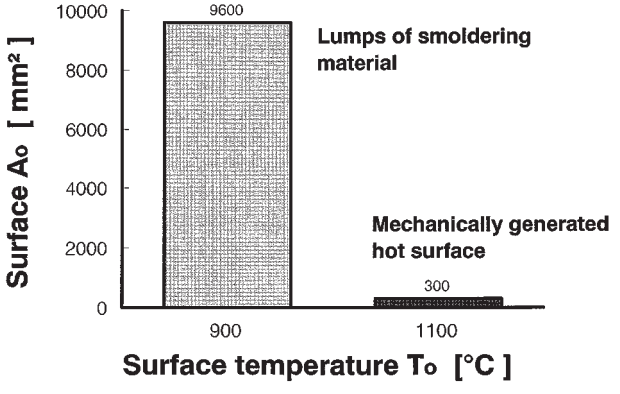


FIG. 26-35 Equivalent energies of mechanically generated hot surfaces and lumps of smoldering material.

- Ground all conductors.
- Ground people.
- Prevent and reduce charging by use of conductive materials.
- Keep conveying speeds low.

If difficulties arise in the avoidance of electrostatic ignition sources, the advice of experts must be sought.

Explosion Protection through Design Measures In applying design measures, the possibility of an explosion is not prevented. Therefore, all exposed equipment has to be built to be explosion pressure resistant, in order to withstand the anticipated explosion pressure. The anticipated explosion pressure may be the maximum explosion overpressure or the maximum reduced explosion overpressure. In addition, any propagation of an explosion to other parts or process areas has to be prevented. Depending on the anticipated explosion pressure, a distinction is made between the following explosion-pressure-resistant designs:

- Capable of withstanding the *maximum* explosion overpressure
- Capable of withstanding an explosion overpressure *reduced* by explosion suppression or explosion venting

The strength of the protected vessels or apparatus may be either explosion pressure resistant or explosion pressure shock resistant.

Constructional measures which restrict the effects of an explosion to a safe level are always necessary when the goal of avoiding explosions cannot be achieved—or at least not with sufficient reliability—through the use of preventive explosion protection. This ensures that people are not injured and further that the protected equipment is usually ready for operation a short time after an explosion. All endangered equipment parts must thus have an *explosion-resistant* construction and withstand the overpressure expected if an explosion occurs. A distinction is made between the *explosion-pressure-resistant* (EPR) and *explosion-pressure-shock-resistant* (EPSR) construction of vessels and silos. Design of the EPR construction is implemented following the calculation and construction directions for pressure vessels, e.g., the ASME pressure vessel code. The EPSR construction allows greater utilization of the material strength (see Figs. 26-36 and 26-37).

For the EPR design, the ASME pressure vessel code requires design to be done at two-thirds of the alloy's yield strength (see Fig.

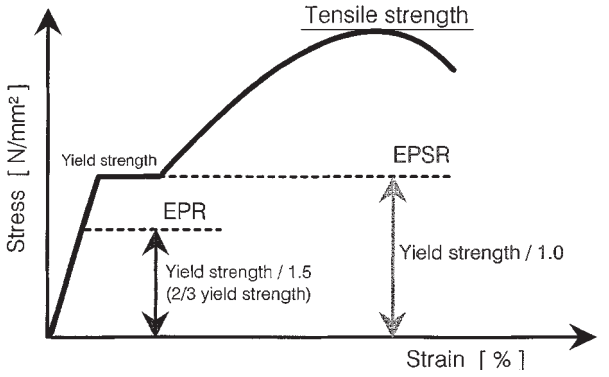


FIG. 26-36 Schematic drawing of stress-strain curve for plate steel.

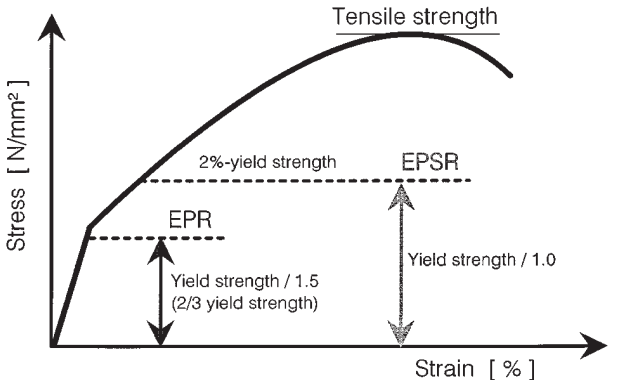


FIG. 26-37 Schematic drawing of stress-strain curve for austenitic stainless steels.

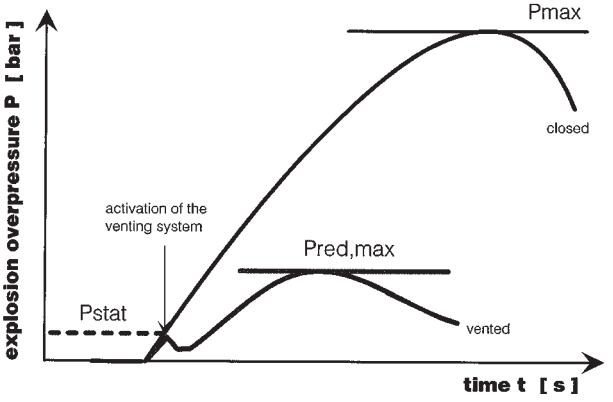


FIG. 26-38 Pressure behavior vs. time for a normal and a vented explosion.

26-36). At such low stresses, there would be no permanent deformation of an ASME code vessel subjected to an explosion overpressure.

For EPSR design, the stress level to contain an explosion is set at the yield strength, a design factor of 1. Thus, for an alloy, the design stress level would be about 1.5 times the ASME code design stress. So a pressure vessel rated at 6 bar for the ASME code (EPR) would have an EPSR rating of 9 bar.

For stainless steel, the stress-strain curve (see Fig. 26-37) has no sharp yield point at the upper stress limit of elastic deformation. Yield strength is generally defined as the stress at 2 percent elongation.

There is still a substantial safety margin up to the ultimate tensile strength, which amounts to 60 to 90 percent, depending on the steel (Kirby, Siwek, "Preventing Failures of Equipment Subject to Explosions," *Chemical Engineering*, June 23, 1986).

Despite the use of explosion-pressure-resistant equipment for the full explosion pressure or other design measures outlined later, everything possible must be done to prevent effective ignition sources, because loss of product and interruption of production are equally undesirable.

Containment (Explosion-Pressure-Resistant Design for Maximum Explosion Overpressure) An explosion-resistant construction is understood to mean the possibility of designing vessels and equipment for the *full maximum explosion overpressure,* which is generally of the order $P_{max} = 9$ bar. The explosion-resistant vessel can then be designed as explosion pressure resistant or explosion pressure shock resistant. This protective measure is generally employed when small vessel volumes need to be protected, such as small filter units, fluidized-bed dryers, cyclones, rotary valves, or mill housings.

One has to consider that all connected devices must also withstand the maximum explosion overpressure.

Explosion Venting (Explosion-Pressure-Resistant Design for Maximum Reduced Explosion Overpressure with Explosion Venting) The concept of explosion venting encompasses all measures used to open the originally closed vessels and equipment either briefly or permanently in a nonhazardous direction following an explosion. *Explosion venting is inadmissible when the escape of toxic or corrosive, irritating, carcinogenic, harmful-to-fruit, or genetically damaging substances is anticipated.* In contrast to the closed vessel, explosions in a vented vessel are characterized by the maximum reduced explosion overpressure $P_{red,max}$ instead of the maximum explosion overpressure P_{max} (see Fig. 26-38) and by the maximum reduced rate of pressure rise $(dP/dt)_{red,max}$ instead of the maximum rate of pressure rise $(dP/dt)_{max}$.

By this method, in general, the expected inherent maximum explosion overpressure of the order $P_{max} = 7$ to 10 bar will be reduced to a value of $P_{red,max} < 2$ bar. In this case, the static activation overpressure of the venting device is $P_{stat} \leq 0.1$ bar. The resulting $P_{red,max}$ may not exceed the design pressure of the equipment. The explosion as such is not prevented; only the dangerous consequences are limited. However, subsequent fires must be expected.

Rupture disks or explosion doors may be used as venting devices. Safety valves are not suitable for this purpose. Obviously, the static activation overpressures P_{stat} of the venting devices have to be equal to or smaller than the strength of the equipment to be protected (corresponding to the $P_{red,max}$).

Rupture disks—for example, plastic foil or aluminum foil—have a low mass and will respond almost without inertia once the activation pressure is exceeded. They can be installed independently of the location and guarantee a dust-tight closure. In case of an explosion they will free the whole area after their destruction. Common materials of construction for rupture disks are metal or alloys. Rupture disks may be combined with signaling devices—for example, ripping wires—which will trigger a shutdown or a controlling mode. Only these rupture disks are to be used that are restrained through design measures.

Explosion doors open in case of an explosion, thereby releasing the vent area. Depending on the application, explosion doors may be selected which remain open or close automatically after releasing the explosion.

The inertia, the opening behavior of the movable cover of the explosion door, and its arrangement (horizontal, vertical) can affect the venting efficiency EF. This results in a higher maximum explosion overpressure $P_{red,max}$ in the protected vessel (see Fig. 26-39).

The venting capability EF and therefore the effective vent area A_w of the explosion door is normally smaller than the capability of a plastic or aluminum foil rupture disk with the same area. Therefore, such devices need testing to determine the mechanical strength before actual use, and the venting capability or the pressure rise, respectively,

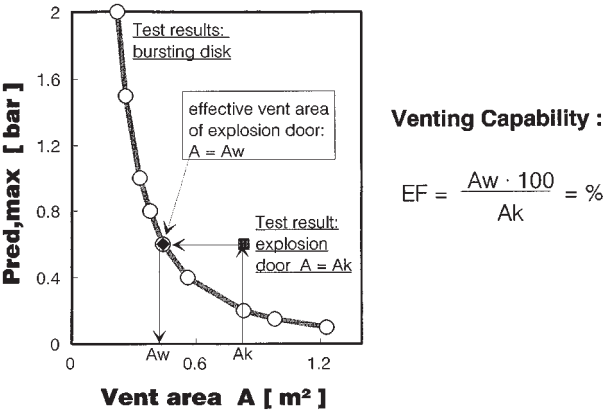


FIG. 26-39 Definition of the venting capability EF of an explosion door in comparison with a plastic foil rupture disk.

have to be chosen relative to the $P_{red,max}$ of the rupture disk of the same area.

When using explosion doors that close the vent area after the explosion, the cooling of the hot gases of combustion may create a vacuum in the vessel, resulting in its deformation. In order to prevent this from happening, vacuum breakers have to be provided.

The vented material discharged from an enclosure during an explosion should be directed to a safe location to avoid injury to personnel and to minimize property damage. If it is necessary to locate equipment that requires explosion venting inside buildings, the vents must not discharge within the building. Flames and pressure waves discharging from the enclosure during venting represent a threat to personnel and could damage other equipment. Therefore, vent ducts should be used to direct vented material from the equipment to the outdoors. If vented equipment is located within buildings, it should be placed close to the exterior walls so that the vent duct will be as short as possible. Vent ducts will significantly increase the pressure development in the equipment during venting. They require at least the same cross section as the vent area and the same design pressure as the protected vessel.

During pressure venting, a recoil is generated by the unburned mixtures and products of combustion flowing through the vent opening. The force bearing on the protected equipment depends on the explosion reduced overpressure and vent area. Not only the recoil force which can be calculated, but also its variation over time, are decisive for the practical design of the structure which supports the explosion-vented vessel. If the influence of the recoil forces is compensated for by arranging vent areas of equal size opposite each other, it is possible for one vent to open before another. Such imbalance should be considered when designing enclosure restraints for resisting thrust force.

For calculation of the venting area, empirical numerical value equations or nomograms can be used (Guideline VDI-3673, *Dust Explosion Venting,* VDI-Verlag, Düsseldorf, 1995; NFPA 68, *Guide for Venting of Deflagrations,* 1994). The calculation methods are not only dependent on the dust explosion constant K_{max}, on the maximum reduced explosion overpressure $P_{red,max}$, on the static activation overpressure P_{stat} of the venting device and on the vessel volume V, but also on the maximum explosion overpressure P_{max}. The vent calculation procedure also makes a distinction between homogeneous dust dispersion (dust-air mixtures generated using the ISO procedure) (ISO Standard 6184/1, *Explosion Protection Systems, Part 1: Determination of Explosion Indices of Combustible Dusts in Air,* Geneva, 1985) and inhomogeneous dust dispersion (dust-air mixtures generated by pneumatic transport) (Siwek, "Dust Explosion Venting for Dusts Pneumatically Conveyed into Vessels," *Plant/Operations Progress,* vol. 8, no. 3, July 1989). When applying the equations between numerical values, it is necessary to decide whether the apparatus being protected is a *cubic* (height-to-diameter ratio less than 2) or an *elongated* vessel (height-to-diameter ratio equal or above 2).

Explosion venting is always accompanied by flame propagation plus pressure consequences in the surrounding areas. The flame length will be larger with a lesser static activation pressure and smaller vent area. Depending on the volume of the protected equipment, it can reach up to 50 m. The pressure effect in the vicinity of the vent area is influenced by the maximum reduced explosion pressure, the vent area, and the vessel volume. A maximum peak overpressure exists at a certain distance from the vent area, which can be calculated. As expected, the distance at which the peak pressure appears increases with increasing vessel volume. For larger distance, this peak pressure decreases.

Based on the hazards due to flame and pressure, personnel should not be endangered by the venting process. Also, the operation of any equipment which is important with regard to safety should not be restricted. This must be considered when designing the plant and may be accomplished by releasing the pressure upward. If this is not feasible, then the vent openings should be placed as high as possible at the side of the vessel. Due to the danger of dust ejection, one has to consider the location of the surface of the dust pile in the vessel. It should never reach the lower edge of the vent opening at maximum operation filling of the vessel.

Among other things, one prerequisite necessary to calculate the pressure relief openings needed on the apparatus is knowledge about the explosion threat definition and venting system hardware definition. The various influences are summarized in Table 26-22.

Explosion Suppression

Explosion-Pressure-Resistant Design for Reduced Maximum Explosion Overpressure with Explosion Suppression Explosion suppression systems provide one means to prevent the buildup of an inadmissibly high pressure, which is the consequence of explosions of combustible material in vessels. They operate by effectively extinguishing explosion flames in the initial stage of the explosion. An explosion of combustible material can generally be regarded as successfully suppressed when the maximum explosion overpressure can be lowered to a reduced explosion overpressure of not more than 1 bar (see Fig. 26-40).

Depending upon the design criteria of the installed suppression system, an unsuppressed explosion overpressure of around 7 to 10 bar is reduced to a suppressed reduced explosion overpressure which lies in the range of $P_{red,max} = 0.2$ to 1 bar. Thus, vessels need to be explosion resistant for an overpressure of maximum 1 bar (ISO Standard 6184/4, *Explosion Protection Systems Part 4: Determination of Efficacy of Explosion Suppression Systems,* Geneva, 1985).

The best advantages of explosion suppression systems is that they can also be used for explosions of combustible materials with toxic properties and that there is no penetration on the location of the process equipment for safe application.

Today, the technology of industrial explosion suppression has evolved to the extent that this technique can and does provide effective industrial safety for almost all industrial processing procedures and for most explosible materials. Developments in explosion suppression hardware—detectors, suppressors, and control equipment, together with new or improved suppressants—provide a versatility of capability which covers all dust explosion classes and process equipment volumes ranging from 0.2 to greater than 1000 m^3. Most significant, the theoretical understanding of explosion propagation and suppression has led to computer-aided design guidance, which has simplified system design.

Explosion suppression systems comprise explosion detectors, pres-

TABLE 26-22 Explosion Venting System Design Parameters

Explosion hazard definition	Venting system definition
Volume of vessel (free volume)	Type of venting device
Shape of vessel (cubic or elongated vessel)	Detection method for triggering a shutdown
Length-to-diameter ratio of vessel	Static activation overpressure P_{stat} of venting device
Strength of vessel	Venting capability of venting device
Type of dust cloud distribution (ISO method/ pneumatic-loading method)	Location of venting device on the vessel
	Position of equipment to be protected in the building
Dust explosibility characteristics:	Length and shape of relief pipe if existent
maximum explosion overpressure P_{max}	Recoil force during venting
maximum explosion constant K_{max}	Duration of recoil force
toxicity of the product	Total transferred impulse
Maximum flame length	
Pressure outside the vent areas	

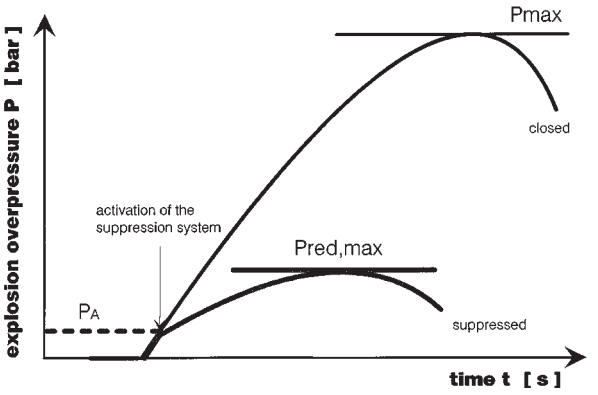


FIG. 26-40 Pressure behavior vs. time for a normal and a suppressed explosion.

surized HRD suppressors (high rate discharge) and a control and monitoring center.

Since the explosion pressure of an incipient explosion in a closed or essentially closed vessel propagates from the explosion epicenter at the speed of sound, pressure detection is an effective means of early explosion detection. Threshold pressure detection using a large area membrane explosion detector provides an electrical contact within milliseconds if the preset overpressure—the system activation pressure, P_a—is exceeded. Such a detector, which responds only to a pressure threshold, is called a *static pressure detector.* It is normal practice to mount two such devices mutually perpendicular and to trigger the explosion suppressors only when both detectors give coincident contact. This obviates the risk of spurious activation as a consequence of incident shock on the detector. Static pressure detectors have been extensively used in industrial applications and have a proven track record. The use of a large-area membrane for such devices ensures that their response is not influenced by the buildup of product or any crusting of product across the sensor surface of the detector. Dependent on selected membrane stiffness, such detectors can be set to operate at pressure thresholds of between 0.05 and 0.7 bar gauge. Static pressure detectors have only limited applicability for process equipment that operates at elevated pressures or that is subjected to significant extraneous pressure excursions.

For such applications, the more sophisticated rate-of-rise membrane pressure detectors must be used. In practice, these *dynamic explosion detectors* have a wide range of applicability. They have both rate-of-rise and pressure threshold trigger points that can be configured specific to the requirement. A timid explosion event may not attain the rate-of-rise criterion, a fact that necessitates a limit pressure threshold to trigger the explosion suppressors. Dynamic explosion detectors provide a means of achieving earlier detection than can be realized with static pressure detectors—and, thus, more effective suppression. Pressure fluctuations as a consequence of normal or abnormal process conditions, such as blocked filters, can be actively discriminated against, thus preventing spurious activation of the suppression system. In larger volumes, since the pressure rises only slowly, care must be taken to set up such detectors to meet appropriate detection response criteria. Dynamic explosion detectors can be used either as static or dynamic explosion detectors or in combination. The two parameters of pressure and time are programmed on-site specific to the installation. The dynamic detector control equipment facilitates event memory, enabling postevent analysis of the pressure domain causing the activation.

Dynamic explosion detectors use a piezoresistive pressure sensor installed behind the large-area, gas-tight, welded membrane. To ensure optimum pressure transference from the membrane to the active sensor element, the space between the membrane and the sensor is filled with a special, highly elastic oil. The construction is such that the dynamic explosion detector can withstand overpressures of 10 bar without any damage or effect on its setup characteristic. The operational range is adjustable between 0 and 5 bar abs. Dynamic explosion detectors are insensitive to shocks and vibration. For many applications, it is thus sufficient to install just one dynamic explosion detector to trigger the explosion suppressors. Since the commercial availability of this new detection method some two years ago, it has a proven performance capability and is being increasingly selected for use in explosion suppression systems.

High rate discharge (HRD) suppressors are available in a range of sizes. Dry powder suppressant is stored in a container, which is pressurized with dry nitrogen to an overpressure of, typically, P_s = 60 to 120 bar. An explosively actuated valve, such as a large-diameter membrane cut by a shaped charge, provides almost instantaneous unimpeded access for the suppressant, which is then expelled by the nitrogen gas and discharged through an appropriate nozzle into the process equipment.

Suppression efficiency is very dependent on the suppressant mass M_s discharge characteristic. This suppressant mass discharge rate is affected by outlet orifice area and propelling agent pressure. HRD suppressors that utilize a large-diameter outlet have superior suppression capability over those that rely on high propelling-agent pressure alone to expel the suppressant charge. The effectiveness of the HRD suppressors against a range of explosion hazards has been fully substantiated. The range of HRD suppressors available provides a wide range of suppression capability. The use of an explosive actuator provides the most effective means of rapid suppressant discharge—typically, less than 2 ms from activation to the start of suppressant release—and ensures the earliest suppression of any explosion event.

In some circumstances, the need to use an explosive actuator to effect suppressant release can be restrictive. HRD suppressors that are actuated by activating an electric initiator, which fractures fast-reacting rupture membrane, have been developed. Thus, within a few milliseconds of activation, an unimpeded opening is provided for the propelling agent to expel the suppressant. Upon fracture of the rupture membrane, the suppressant flows from the pressurized HRD suppressor through the outlet into a specifically engineered suppressant distribution piping system. These new types of HRD suppressors have, in order of magnitude, the same valve opening time and the same outlet orifice and provide an alternative means of suppressant deployment where explosive actuators are not admissible.

The HRD suppressor discharge elbow and the discharge nozzle have an important influence on suppression effectiveness. A nozzle that achieves a wide angular dispersion of suppressant is most effective for explosion suppression in smaller volumes, but the limited suppressant throw that results reduces its effectiveness for larger-volume explosion suppression. Irrespective of nozzle type, the suppressed explosion with an elbow (the HRD suppressor is mounted on the side of a vessel) is higher, demonstrating the effect of an elbow in slowing suppressant delivery into the vessel. On the other hand, if the HRD suppressor is mounted on the top (without an elbow) of the same vessel, a clearly more effective suppression is achieved, because no elbow is slowing the delivery of the suppressant. A normal arrangement of the nozzle for the distribution of the suppressant is protruding into the protected equipment. In practice, this is very often undesirable, especially if the enclosure handles dust with frequent production changes. To avoid disturbance of the production process (cleaning, product deposits, hygiene) by projection of the suppressant dispersion system into the protected vessel, movable, so-called telescopic nozzles (see Fig. 26-41) must be installed. Initially, the nozzle arrangement is located outside the vessel to be protected, separated from the latter by a membrane. This membrane does not reduce the HRD effectiveness. In applications where a true hygienic seal is required or where high-pressure excursions are to be expected, frangible metal or carbon discs are used. Such hermetic seals do slow, to a degree, the suppressant discharge from an HRD suppressor and this must be allowed for in the design. In the event of an explosion, once the HRD suppressor is activated, the nozzle is propelled forward by the suppressor pressure, rupturing the membrane and locating in its operating position to ensure effective suppressant deployment.

The most widely deployed industrial explosion suppressant is monoammonium phosphate powder (MAP). This suppressant has a wide range of effectiveness. However, it can prove to be a contaminant, necessitating stringent clean-down procedures after a suppressed explosion incident. This limitation is overcome by selecting a sodium

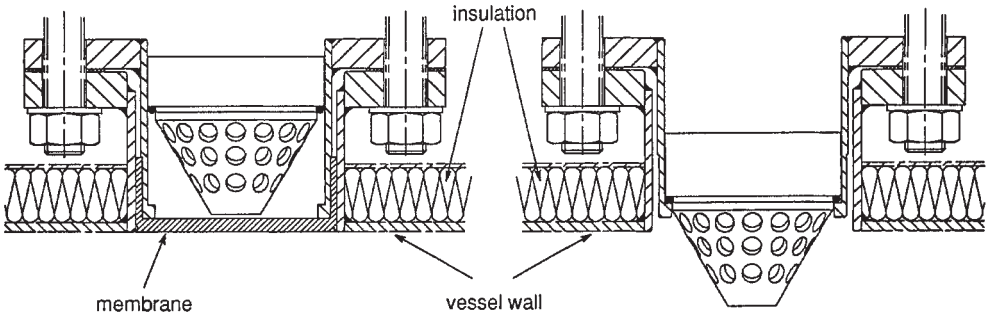


FIG. 26-41 Example for a telescopic nozzle arrangement.

bicarbonate (NaBi)–based dry powder suppressant. Food-grade compatible and readily water-soluble proprietary sodium bicarbonate suppressants are increasingly being used to protect industrial processes for manufacturing foodstuffs and pharmaceuticals. All types of suppressant have a fine particle size distribution—high specific surface—and flow additives to minimize particle agglomeration.

The sodium bicarbonate suppressant attains almost equivalence in performance with the monoammonium phosphate powder. Water has proven to be a very effective suppressant of dust, especially grain and fodder dusts. A suppressant is regarded as being very effective when an increase of the activation pressure P_a of the explosion system leads to an increase as small as possible in the maximum reduced explosion overpressure $P_{red,max}$ (see Fig. 26-42).

A recent development postulates that superheated water is a more effective suppressant than water alone because, on discharge, release of the superheated water charge results in partial flash vaporization of the water droplets to steam with a consequential fragmentation of the droplets, thus achieving a higher specific surface for effective suppression. At high temperature, effective suppression is achieved—but the effectiveness is very dependent on the control of temperature. The complication of maintaining the water suppressant charge at a fixed and controlled elevated temperature negates this option for most practical purposes.

Explosion suppression control equipment has traditionally been simple in operation, maintaining the highest level of reliability. In some applications, advantage can be achieved by introducing a level of intelligence and interpretation into the control equipment signal processing. New control and annunciation central control systems employ state-of-the-art electronics. Often called an *alarm center,* such a watchdog or operational center of any explosion suppression system is modular in construction. Individual modular "cards" can be plugged in, to accommodate the requirements of the full explosion protection system. Alarm centers are futureproof—they can be added to as the system expands. An alarm center records and monitors the signals transmitted by explosion pressure detectors, spark and flame detectors, temperature, and other safety sensors. Dependent on configuration, by interrogation and interpretation of the detector/sensor data, the alarm center selectively controls the actuation of explosion suppressors, extinguishing barriers, fast-shutting isolation valves, process equipment shutdown, water spray or extinguishant release, and all audible and visual alarms. System internal monitoring gives fault indication in the event of device or field wiring defect, and alarm and fault relay contacts can be connected as appropriate. Standby power is facilitated from an independent, monitored battery such that full explosion protection is assured during any power failure. System isolation to facilitate safe working on or in a protected vessel is standard, and remote actuation of key functions and system status record, via an on-line printer, are facilitated as options. Zoning of HRD suppressors enables the control system to ensure that suppressors deployed to inject extinguishant that is to act as an extinguishing barrier, and thus prevent flame propagation down a duct, are used to maximum effect.

A suitable locking mechanism must ensure that the production plant can be started up again only if the explosion suppression system is fully operational. The alarm center must be designed so that, if work is performed within the protected vessel, the detectors can be made inoperable and secured against inadvertent triggering.

Design of explosion suppression systems is clearly complex, since the effectiveness of an explosion suppression system is dependent on a large number of parameters. One hypothesis of suppression system design identifies a limiting combustion wave adiabatic flame temperature, below which combustion reactions are not sustained. Suppression is thus attained, provided that sufficient thermal quenching results in depression of the combustion wave temperature below this critical value. This hypothesis identifies the need to deliver greater than a critical mass of suppressant into the enveloping fireball to effect suppression (see Fig. 26-43).

If the suppression criterion is not met, the consequence is a failed

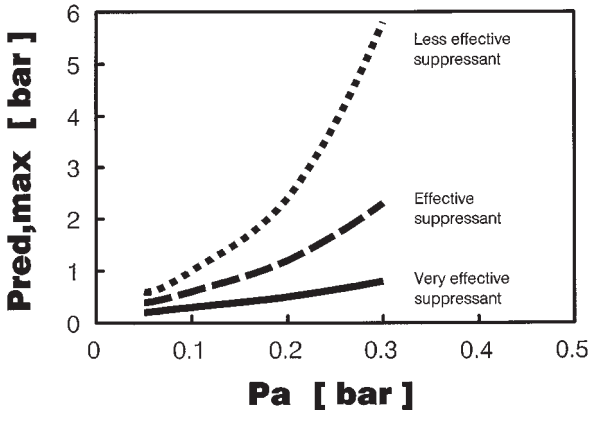


FIG. 26-42 Influence of the activation overpressure P_a and suppressant upon the effectiveness of a suppression system (constant test condition).

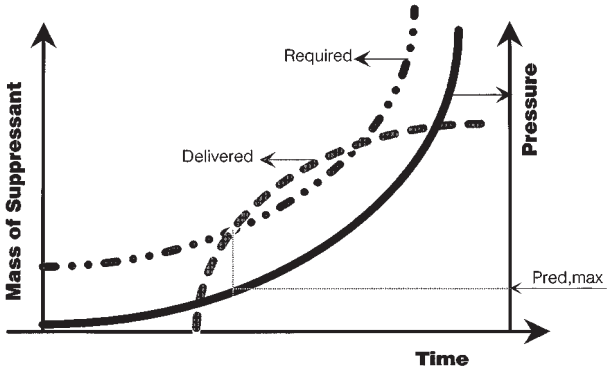


FIG. 26-43 Design basis for explosion suppression.

TABLE 26-23 Suppression System Design Parameters

Explosion hazard definition	Suppression system hardware definition
Volume of vessel (free volume V)	Type of explosion suppressant and its suppression efficiency
Shape of vessel (area and aspect ratio)	Type of HRD suppressors: number and free volume of HRD suppressors and the outlet diameter and valve opening time
Type of dust cloud distribution (ISO method/pneumatic-loading method)	Suppressant charge and propelling agent pressure
Dust explosibility characteristics:	Fittings: elbow and/or stub pipe and type of nozzle
Maximum explosion overpressure P_{max}	Type of explosion detector(s): dynamic or threshold pressure, UV or IR radiation, effective system activation overpressure P_a
Maximum explosion constant K_{max}	Hardware deployment: location of HRD suppressor(s) on vessel
Minimum ignition temperature MIT	

suppression, in which combustion is not arrested and high explosion pressures must be anticipated.

For any proposed suppression system design, it is necessary to ascribe with confidence an effective worst-case suppressed maximum explosion overpressure $P_{red,max}$. Provided that the suppressed explosion overpressure is less than the process equipment pressure shock resistance and provided further that this projected suppression is achieved with a sufficient margin of safety, explosion protection security is assured. These two criteria are mutually independent, but *both* must be satisfied if a suppression system is to be deployed to provide industrial explosion protection.

Suppression system design parameters fall into the two categories of explosion threat definition and suppression system hardware definition. The various influences are summarized in Table 26-23.

The type of HRD suppressors and their number and, hence, the extinguishing agent requirement can be determined with the aid of nomograms or simple numerical value equations developed from numerous experiments and model calculations (Siwek, Moore, "Extended Design Practice for Explosion Suppression Systems," *Proc. 8th Int. Symposium Loss Prevention and Safety Promotion in the Process Industries,* Antwerp, Elsevier, Amsterdam, 1995). As dry powder extinguishing agents are predominately used in industrial practice, the calculation fundamentals for the extinguishing agent requirement are limited to these extinguishing powders.

To achieve an effective and practical application, HRD suppressors of different sizes must be used for the different sizes and geometry of the protected vessels.

Of practical benefit to the processing industry is the combination technology of explosion venting and explosion suppression. It is evident that the deployment of a small explosion vent results in a useful further reduction in the resultant suppressed explosion pressure. Tests have shown that, provided the HRD suppressor is located such that the suppressant is deployed across the vent aperture, no flame ejection results. It is often the case in practical situations, where neither venting nor suppression alone can provide an appropriate safety solution, that, by combining the technologies, safety is assured. Where the primary protection means is explosion suppression, the addition of vents results in a lowering of the achievable reduced explosion pressure. Where the primary protection means is explosion venting, the addition of HRD suppressors reduces the vented explosion pressure. Results have shown that with high-K_{max} aluminum dust explosions, the reduced (vented) explosion pressure can be further reduced by more than 50 percent by the addition of HRD suppressors, although flame extinction is not achieved against the explosion threat. Tests on silos confirm that the deployment of an extinguishing barrier across the top of a silo fitted with explosion vents can prevent a secondary dust explosion in the room above the silo. This strategic use of extinguishing barriers ensures that flame ejection from a vented explosion incident is minimized. Similarly, extinguishing barriers in the vent pipes of relief venting systems minimize any flame ejection.

The combination of explosion safety technologies can provide more effective safety than is possible by deploying just one safety measure. In this respect, the improved capabilities of explosion suppression further enhance overall explosion protection capability.

Comparison of Explosion Protection Design Measures In Table 26-24, comparison is made of the explosion protection design measures of containment, explosion venting, and explosion suppression. Regarding the effectiveness of the different explosion design measures, all three techniques are equal if the design of these measures is performed properly.

Explosion Isolation For all equipment systems protected by design safety measures it is also necessary to prevent the propagation of an explosion from these protected vessels into operating areas or equipment connected via interconnecting pipeline. Such an approach is referred to as *explosion isolation.*

To prevent an explosion occurring in, for example, a constructional protected installation from spreading through a pipeline ($l > 6$ m) to part of the installation fitted with preventive explosion protection, explosion isolation measures (see Fig. 26-44) must be implemented. As explosions are generally propagated by *flames* and not by the pressure waves, it is especially important to detect, extinguish, or block this flame front at an early stage, i.e., to isolate or disengage the explosion. If there is no explosion isolation, the flame issuing from the equipment—for example, from the equipment protected through design (equipment part 1)—through the connecting pipeline comes into contact with a highly turbulent precompressed mixture in the equipment with preventive protection (equipment part 2). The mixture will ignite in an instant and explode; a large increase in the rate of

TABLE 26-24 Comparison of Explosion Protection Design Measures

	Containment	Explosion venting	Explosion suppression
Pressure resistance P	7–10 bar	Without relief pipe, up to 2 bar With relief pipe, up to 4 bar	St 1 up to 0.5 bar St 2+3 up to 1.0 bar
Location	Independent	Dependent	Independent
Limits of application	Products which decompose spontaneously	Toxic products and products which decompose spontaneously	Products which decompose spontaneously, metal dust hazard
Environmentally friendly	Yes	No (flame, pressure, and product)	Yes
Loss of material*	+++++	+++++	++
Maintenance requirements†	++++	++++	+++++

*The loss of material by using containment and explosion venting is always much greater than that by using explosion suppression.

†To ensure the reliability of explosion protection devices, regular servicing and maintenance are required. The nature and time intervals of these activities depend on technical specifications and on the plant situation. Normally, after commissioning of the plant, inspections are carried out in comparatively short intervals, e.g., every month. Positive experience may subsequently provide for longer service intervals (every three months). It is recommended to contract service and maintenance to reliable, specialized companies.

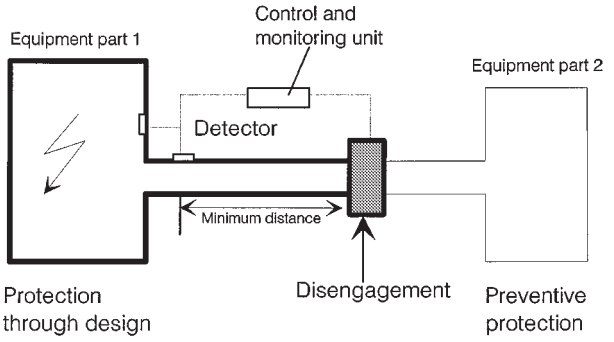


FIG. 26-44 Principle of the constructional measure explosion isolation.

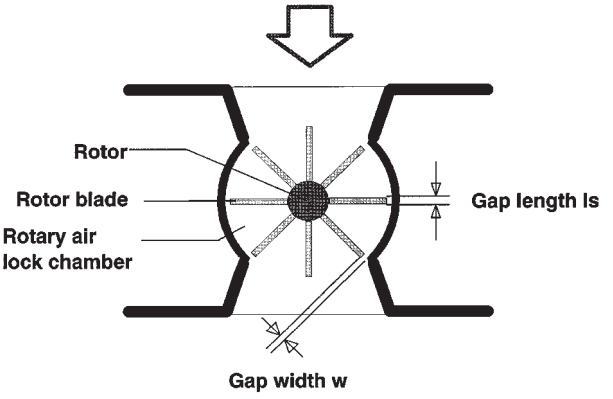


FIG. 26-45 Design features of a rotary valve.

combustion reaction and, naturally, in the reduced explosion overpressure is the result. The equipment in question may be destroyed.

The mechanical flame barriers, which are used for explosion isolation of flammable gas and solvent vapor explosions, are very susceptible to the action of dirt and, with one exception, are thus *not suitable for dust-carrying* pipelines. The exception involves the *rotary valve* (see Fig. 26-45), which is based on the flame-quenching effect through narrow gaps and is mainly used at product charging and discharging points.

The size of the gap between the rotor blades and the housing depends on the construction and is important for the ignition breakthrough protection of the rotary valve. The maximum gap width of combustible dusts, like that of flammable gases, lies in the millimeter range. With knowledge of the ignitability of a dust, the gap length, and the number of constantly diametrically opposed rotor blades, a nomogram can be used to determine the maximum admissible gap between the blades and the inner wall of the rotary valve. In the event of an explosion, the valve must be automatically stopped to prevent any subsequent upstream fire or explosion due to passage of smoldering material or burning product through the valve. As a rule of thumb, it was found for normal organic dusts that the ignition cutout of rotary air locks is effective when three rotor blades on each side are diametrically opposed, provided that the blades are made of metal and the gap between the tip of the rotor blade and the housing is ≤0.2 mm (Siwek, "New Knowledge About Rotary Air Locks in Preventing Dust Ignition Breakthrough," *Plant/Operating Progress* vol. 8, no. 3, July 1989).

An *extinguishing barrier* comprises an optical flame sensor and an HRD suppressor located downstream of the detected flame front. The effectiveness of an extinguishing barrier is based on its ability to detect an explosion in a pipeline by means of an optical flame detector whose tripping signal is amplified and then very quickly actuates the detonator-actuated valves of the pressurized HRD suppressors. The extinguishing agent—preferably extinguishing powder—is discharged into the pipeline and forms a thick blanket, which extinguishes the incipient flame. There is a definite distance between the installation sites of the optical detector and the extinguishing barrier to ensure that the extinguishing agent acts directly on the flame. The amount of extinguishing agent required depends on the nature of the combustible dusts, the nominal diameter of the protected pipeline, the explosion velocity, and the maximum reduced explosion overpressure in the vessel. This type of barrier does not impede product throughput down the pipeline.

The alternative to the extinguishing barrier is the *rapid-action explosion isolation gate valve.* These valves must be tested for ignition breakthrough protection and pressure rating in dust explosions. They can meet these requirements for dust explosions and are effective against dust explosions at shorter distances than for gas explosions. When rapid-action gate valves are used, a dust explosion approaching the installation site in the pipeline is detected by an optical sensor and the closing process is initiated by a triggering mechanism. The closing time depends on the nominal width of the rapid-action devices and is generally less than 50 ms.

Explosion isolation can also be effected by *rapid action barrier valves.* At present, they can be arranged only in horizontal pipelines and are suitable, in general, only for streams with a small amount of dust. Such valves are thus frequently used to protect ventilation lines. As a certain explosion overpressure is necessary to close such valves, a distinction is made between *self-actuated* and *externally actuated* barrier valves (Fig. 26-46).

The interior of the barrier valve contains a valve cone mounted in

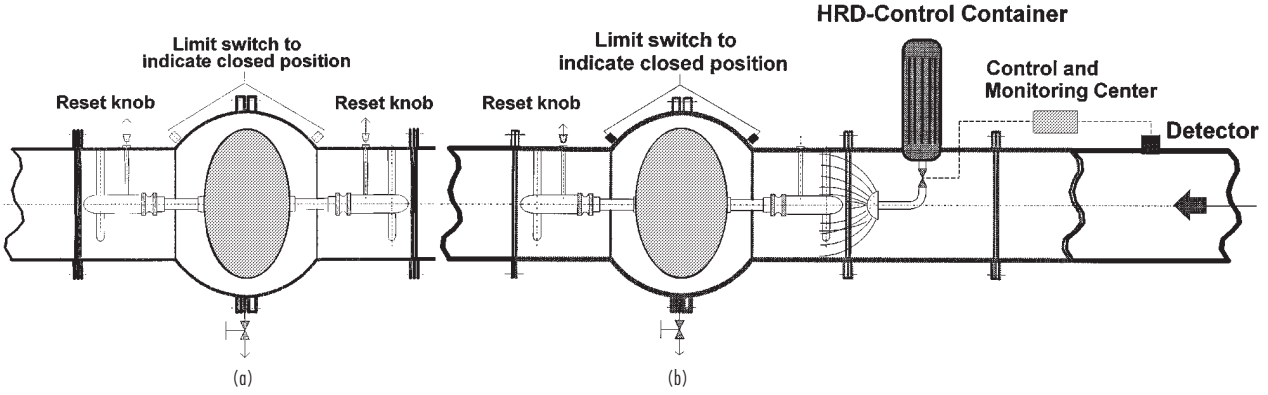


FIG. 26-46 Rapid-action barrier valves: (*a*) self-actuated; (*b*) externally actuated.

spherical sockets, which can be moved axially in both directions; it is held in its middle position by springs. The spring tension is set for a maximum flow velocity of 25 $m \cdot s^{-1}$, based on the pipeline cross section. If an explosion occurs, the valve closes automatically, owing to the kinetic energy of the pressure wave preceding the flame front. Here, either the explosion velocity must be greater than 25 $m \cdot s^{-1}$ or the pressure difference in front of and behind the valve greater than 0.1 bar. The valve cone is pressed onto a rubberized valve seat on closing and held in place by a retaining device. It is released from outside. The self-actuating barrier valve (Fig. 26-46*a*) functions in both directions. Barrier valves can also be operated by a sensor-controlled auxiliary gas flow (jets of nitrogen from control containers onto the valve cone) in the direction of the pipe axis via a hemispherical nozzle (Fig. 26-46*b*). These are installed when low explosion overpressures are expected and, consequently, ignition breakthrough of an explosion through the installation site can occur with a self-actuated valve. The externally actuated barrier valve functions in one direction only.

Particularly reasonably priced explosion isolation of systems involves the use of a *relief pipe* with which the flow direction can be diverted by 180°. It prevents flame jet ignition with precompression in constructionally protected equipment. If suction is present, explosion propagation can occur. To prevent this, the use of an additional extinguishing barrier or a rapid-action gate valve is necessary. If a diverter is installed where positive pressure feed is given, then the diverter is, in general, safe against an explosion propagation.

Product removal mechanisms from apparatuses that are explosion resistant can be protected with a *double-slide* system. Here, the slides must be at least as resistant as the apparatuses. By means of proper control, it must be assured that a slide is always closed.

Finally, it must be pointed out that all devices suitable for use in explosion isolation—or, quite generally, all explosion protection devices used in practice—may be used only when their *pressure rating, ignition breakthrough protection,* and *reliability* have been proven in suitable investigations by competent bodies.

STATIC ELECTRICITY

Nomenclature

C	Capacitance, farads
C/kg	Charge density, coulombs/kg
C/m^2	Surface charge density, coulombs/m^2
F	Farads
J	Energy, joules
K_e	Relative dielectric constant, dimensionless
kV/m	Electric field intensity, kilovolts/meter
m	Meters
MIE	Minimum ignition energy, mJ
mJ	Millijoules
Ω^2	Resistivity value, ohms per square, usually used for fabrics and films
pS	Conductivity, picosiemens
pS/m	Electrical conductivity of liquid
RH	Relative humidity, %
S	Siemens (formerly mho)
T	Time, s
V	Electrical potential, volts
V/m	Electric field intensity, volts/meter

General References: Bailey, "Charging of Solids and Powders," *J. Electrostatics* **30,** pp. 167–180, 1993. Blythe and Reddish, "Charges on Powders and Bulking Effects," *Electrostatics 1979,* Inst. Phys. Conf. Ser. No. 48, London, pp. 107–114, 1979. Finke, "Electrostatic Effects of Charged Steam Jets," *J. Electrostatics* **23,** pp. 69–78, 1989. *Generation and Control of Static Electricity,* Scientific Circular No. 803, National Paint and Coatings Association, Washington, D.C., 1988. Gibson and Lloyd, "Incendivity of Discharges from Electrostatically Charged Plastics," *Brit. J. Appl. Phys.* **16,** pp. 1619–1631, 1965. Owens, "Ignition Hazards of Charged Dielectrics in Flammable Environments," *IEEE Trans. Ind. Applic., IA-20,* no. 6, Nov./Dec. 1984. *Plant/Operations Progress* **7,** no. 1, Jan. 1988. Entire issue devoted to papers on static electricity, presented at AIChE meeting, Minneapolis, Minn., August 1987. Post, Glor et al., "The Avoidance of Ignition Hazards Due to Electrostatic Charges Arising During the Spraying of Liquids under High Pressure," *J. Electrostatics* **23,** pp. 99–110, 1989. *Protection Against Ignitions Arising Out of Static, Lightning and Stray Currents,* American Petroleum Institute Recommended Practice 2003, 1991.

Introduction Spark-ignition hazards must be considered whenever static charges may accumulate in an environment that contains a flammable gas, liquid, or dust. The need for electrical bonding and grounding of conductive process equipment in hazardous (classified) locations is widely recognized. Less well understood are the ignition hazards associated with static charges on poorly conductive, flammable liquids, solids, and powders. Static charges, generated on these materials by normal handling and processing, cannot be conducted to ground quickly and may cause hazardous charge accumulations. The electric fields associated with these charges may stress the surrounding air sufficiently to cause breakdown by some type of electrical discharge.

Electrical discharges from poorly conductive materials take several forms, each differing in its ability to ignite flammable mixtures. It is not possible to calculate the incendivity of these discharges, because of their varying time and spatial distributions. Several engineering rules of thumb for estimating the relative hazard of these discharges are discussed in the following.

Any analysis of static-ignition hazard should start with data on the ignition sensitivity of the particular flammable material at its most flammable concentration in air, i.e., its *minimum ignition energy* (MIE). This is especially important for dusts. It is prudent to determine this value on fines of the specific dust of interest, rather than to rely on published data. Hybrid mixtures (i.e., mixtures of dust and flammable vapor for which vapor concentrations may be below the lower explosive limit) can be ignited by smaller discharge energies than might be expected.

The key to safe operation is to provide an adequate means of charge dissipation from charged materials to ground. This requires mobility of charges in or on the charged material *plus* electrical continuity from the material to ground.

Definitions

antistatic material One with an electrical resistivity that is low enough to make it incapable of accumulating hazardous concentrations of static charges when grounded.

bonding A method of providing electrical continuity between two or more conductive objects to prevent electrical sparking between them.

charge relaxation time The time required for the charge in a liquid or on a solid material to dissipate to 36.8 percent of its initial value when the material is grounded.

electrical discharge A current flow, which occurs when the electrical field strength exceeds the breakdown value in a medium such as air.

flammable mixture A mixture of a gas, mist, or dust in air, which is within its flammable range.

grounding A special form of bonding, in which a conductive object is electrically connected to (earth) ground.

incendive discharge Any discharge that has sufficient energy to ignite a specified flammable mixture.

minimum ignition energy The smallest amount of spark energy that has been found capable of igniting a specified flammable mixture in a standard test (Calcote, Gregory et al., "Spark Ignition; Effect of Molecular Structure," *Industrial and Engineering Chemistry* **44,** no. 11, 1952).

Electrostatic Charging

Types The primary cause of electrostatic charging is *contact electrification,* which takes place when two different materials are brought into contact and separated. Other causes include induction charging, the formation of sprays, and impingement of charged mist on an ungrounded conductor.

Contact Electrification This form of charging involves the contact and separation of solid-solid, solid-liquid, or liquid-liquid surfaces. Pure gases do *not* cause charging unless they carry droplets or dust particles.

Efforts to quantify the magnitude and polarity of contact charging have had limited success, because minute variations in the types and concentrations of contaminants exert a large influence on charge sep-

aration. Even like solid-solid surfaces can produce significant charge separation. The charge density on separated solid-solid surfaces is, usually, very nonuniform. Each surface may contain both + and – polarity charges, with more of one polarity than the other. After separation, the charges will dissipate slowly or rapidly, depending upon the electrical resistivity of the material and the presence of a path to ground.

Contact electrification at liquid-liquid and liquid-solid interfaces is attributed to the absorption of ions of one polarity by one surface. Ions of opposite polarity form a diffuse layer near the interface. If the diffuse layer is carried along by moving liquid, as in a pipeline, the flowing charges (called a *streaming current*) may create a sparking hazard downstream. One protective measure is to keep the charged liquid in a closed, grounded system (a *relaxation chamber*) long enough to allow safe dissipation of the charges.

The magnitude of the streaming current in any given situation is not readily calculated. Equations, derived experimentally for some liquids (Bustin and Dukek, *Electrostatic Hazards in the Petroleum Industry,* Research Studies Press, Letchworth, England, 1983) show that flow velocity has the greatest influence on pipeline charging. Streaming currents can be limited to safe levels by limiting velocities to less than 1 m/s.

Charge Induction This charging takes place when a conducting object is exposed to electric fields from other charged objects. Examples include the induction charging of a human body by clothing, the charging of a conductive liquid in a charged, plastic container, or the charging of the conductive coating on one-side-metallized film by static charges on the uncoated surface.

Although charge induction can take place whether or not the conductive object is grounded, a sparking hazard is present only if the conductor is not grounded. This phenomenon can convert a relatively innocuous charge buildup on a nonconductor into a serious sparking hazard by raising the potential of the conductor above ground (Owens, "Spark Ignition Hazards Caused by Charge Induction," *Plant/Operations Progress* **7,** no. 1, pp. 37–39, 1988).

Spraying Droplets, formed by spray nozzles, tend to be highly charged even if the conductivity of the liquid is high. Because there is no path to ground from the droplets, their charges can accumulate on an ungrounded conductor to cause sparking. If flammable vapor is present, as in some tank-cleaning operations, it is essential that the spray nozzle and tank be bonded or separately grounded. It is safer to use a nonflammable cleaning solvent or one that has a conductivity greater than 1000 pS/m.

Mists Although charged mists are unable to cause ignition of flammable vapor by self-generated sparking, it is important that the mist not impinge upon an ungrounded conductor.

Charge Dissipation

General It is an experimental fact that charged objects exert a force on other charged objects. This behavior is explained by the presence of an *electric field,* i.e., electric lines of force, each of which emanates from a + charge and terminates on a – charge. The *magnitude* of the field is defined as the force on a unit test charge placed at the point of interest. The *direction* of the field is the direction of the force on a + test charge placed at the point.

Static charge generation causes an ignition hazard only if the accumulated charges create an electric field sufficient to produce an electrical discharge in a flammable atmosphere. In most processes, this means that the electric field intensity at some location must reach the breakdown strength of air (nominally 3×10^6 V/m). The objective of static-control measures is to ensure that electric field intensities cannot reach this value.

Conductors Bonding and grounding are the primary means of dissipating charges from conductive objects. Bonding clamps should be of the single-point type, which bites through oxide or enamel coatings to make contact with the bare metal. Owing to the sturdy construction of bonding clamps and cables, their initial resistance is less than 1 Ω.

It is good practice to visually inspect the condition of bonding cables during each use and to measure the resistance of temporary bonding cables, at least annually, to confirm that it is less than, say, 25 Ω.

Antistatic Materials These materials allow static charges to dissipate without causing hazardous accumulations. Charge dissipation normally takes place by conduction along the material to ground. The antistatic behavior of such materials is measured, at a controlled temperature and relative humidity, in terms of Ω^2 (ohms per square) of *electrical surface resistivity.* Resistivity values needed for safety depend upon the rate of charge generation, but are typically in the range of 10^8 to 10^{11} Ω^2 (ohms per square) for fabrics and films (ASTM Standard Test Method D-257-78, *DC Resistance or Conductance of Insulating Materials*).

An alternate test for antistatic performance is the *charge-decay* test, in which the time of charge-decay is measured after 5 kV have been applied to the specimen (Federal Test Method 101C, Method 4046.1). For many purposes, a charge-decay time of 0.5 s to 500 V, measured at the RH in end use, indicates good antistatic performance.

The electrical surface resistivity and charge-decay time of most materials vary substantially with the relative humidity. It is important that materials be tested at the lowest RH expected in use. Items that are antistatic at 50 percent RH may *not* be antistatic at 20 percent RH.

Some fabrics contain a small percentage of conductive fibers or staple, which limit charge accumulation by *air ionization.* These fabrics do not depend upon conduction of static charges and may not appear conductive in the electrical resistivity or the charge-decay test. Antistatic performance is not humidity-dependent. Work is under way to develop a standard test for these fabrics (Nelson, Rogers, and Gilmartin, "Antistatic Mechanisms Associated with FIBC Fabrics Containing Conductive Fibers," *J. Electrostatics* **30,** pp. 135–148, 1993).

Liquids The rate of dissipation of charges in a liquid, assuming that its conductivity and dielectric permittivity are constant, can be expressed as:

$$T = 8.85 \frac{K_e}{C} \tag{26-52}$$

where T = time required for the charge density to dissipate to 36.8% of its initial value, s
K_e = relative dielectric constant of the liquid, dimensionless
C = electrical conductivity of the liquid, pS/m

Flammable liquids are considered particularly static-prone if their electrical conductivity is within the range of 0.1 to 10 pS/m. If no particulates or immiscible liquid are present, these products are considered safe when their conductivity has been raised to 50 pS/m or higher. Blending operations or other two-phase mixing may cause such a high rate of charging that a conductivity of at least 1000 pS/m is needed for safe charge dissipation (British Standard 5958, part 1, *Control of Undesirable Static Electricity,* para. 8, 1991).

Electrostatic Discharges An electrostatic discharge takes place when a gas or vapor-air mixture is stressed, electrically, to its breakdown value. Depending upon the specific circumstances, the breakdown appears as one of four types of discharges, which vary greatly in origin, appearance, duration, and incendivity.

Sparks Spark discharges are most common between solid conductors, although one electrode may be a conductive liquid. They appear as a narrow, luminous channel, and carry a large peak current for a few microseconds or less. Sparks are the only form of discharge for which a maximum spark energy can be calculated, using the expression:

$$J = 0.5\, C \cdot V^2 \tag{26-53}$$

where J = total stored energy dissipated, J
C = capacitance of charged system, F
V = initial potential difference between electrodes

Incident investigations often require that an estimate be made of the possible spark energy from an ungrounded conductor. If the discharge path contains significant resistance, some of the stored energy is dissipated in the resistance, thereby lowering the energy in the spark gap.

Corona A corona is generated when a highly nonuniform electric field of sufficient strength terminates on a conductor that has a small radius of curvature (i.e., a point, wire, or knife-edge). The luminous

(breakdown) region is confined to a small volume near the corona electrode. Because of their small peak currents and long duration, corona discharges do not have sufficient energy to ignite most flammable materials found in industry (i.e., materials having a minimum ignition energy above 0.2 mJ). For this reason, they can be used safely as static neutralizers in most hazardous (classified) locations. Corona discharges *can* ignite hydrogen-air and oxygen-enriched, gas mixtures.

Brush Discharges These discharges take place between conductors and charged nonconductors, where the radius of curvature of the conductor is too large for corona generation. The name refers to the brushlike appearance of the discharge, which spreads from the conductor to discrete areas on the nonconductor. The brush discharge may have a hot "stem" near the conductor which, though short-lived, may cause ignition by raising the temperature of the flammable mixture to its autoignition value (Norberg, "Modeling Current Pulse Shape and Energy in Surface Discharges," *IEEE Trans. Ind. Applic.* **28,** no. 3, pp. 498–503, May/June 1992).

Brush discharges from – charged nonconductors have been found more incendive than those from + charged nonconductors. Spark energies from brush discharges are limited to less than 4 mJ, because charges from a small area on the nonconductor are able to participate in the spark. Most dust-air mixtures cannot be ignited by brush discharges because their MIE exceeds 4 mJ (Gibson, "Electrostatic Hazards—A Review of Modern Trends," *Electrostatics 1983,* Inst. Phys. Conf. Ser. No. 66, London, pp. 1–11, 1983).

Surface charge densities cannot exceed the theoretical value of 2.7×10^{-5} C/m^2 (set by air breakdown) and will normally be less than 1.5×10^{-5} C/m^2.

Propagating Brush Discharges These discharges are much less common than brush discharges. They sometimes occur when a nonconductive film or plastic layer acquires a double layer of charges, i.e., + polarity charges on one surface and – polarity charges on the opposite surface. Surface charge densities can be very large, because they are not limited by the breakdown of air.

The double layer can be formed by contact (*triboelectric*) charging of one surface of the nonconductor, while the opposite surface is in contact with a conductor, e.g., a nonconductive coating on a metal chute or a plastic-lined, metal pipe for powders. A less frequent cause is contact-charging of one surface, while air ions are supplied to the opposite surface.

Investigations by Glor ("Discharges and Hazards Associated with the Handling of Powders," *Electrostatics 1987,* Inst. Phys. Conf. Ser. No. 85, pp. 207–216, 1987) and others conclude that propagating brush discharges require surface charge densities above 2.7×10^{-4} C/m^2. In addition, the breakdown voltage of the insulating layer must be greater than 4 kV for a thickness of 10 μm, or 8 kV for a thickness of 200 μm.

If a conductor approaches the charged surface, the electric field will produce air ionization at the surface, which creates a semiconductive layer, thereby allowing charges from a large area to participate in a single discharge. Because these discharges can have energies of 1 J or more, they are very hazardous in a flammable environment. They may also cause severe shocks to operators who reach into a nonconductive container that is receiving charged powder, pellets, or fibers.

Causes of Hazardous Discharges with Liquids

Self-Generated Discharges Vapor-air mixtures can be ignited by sparks from highly charged liquids. It is said that such liquids "carry their own match." Typical causes of such charging for poorly conductive (<50 pS/m) liquids include:

1. High-velocity flow
2. Free-fall/splashing
3. Filtering
4. Spraying
5. Agitation with air
6. Blending with powder
7. Settling of an immiscible liquid (e.g., water in gasoline)
8. Liquid sampling from pressurized lines, using ungrounded or nonconductive containers

Conductive liquids in nonconductive containers may cause sparking if the outside of the container is charged by rubbing.

External Causes of Incendive Static Discharges

1. Sparks from ungrounded persons
2. Brush discharges from flexible, intermediate, bulk containers (FIBCs), plastic bags, stretch wrap, or other plastic film
3. Propagating brush discharges from metal-backed plastic film or linings

Powders Contact charging of powders occurs whenever particles move, relative to one another or to a third surface. Significant charging can be generated by operations such as grinding, mixing, sieving, pouring, and pneumatic transfer. Maximum charge densities (C/kg) on airborne powder increase as particle size decreases, because of larger surface/mass ratios. Dry fines can be expected to charge more highly than those containing moisture. While suspended in air, charged powder poses an ignition risk only if nonconductive piping is used in the conveying lines or if conductive piping is not properly bonded.

The *collected* powder may accumulate so much charge per unit volume that the associated electric field strength causes breakdown of the surrounding air in the form of corona or a brush discharge. For receiving containers larger than about 1 m^3, so-called bulking discharges may be present, with energies of up to 10 mJ. The ignition hazard from bulking discharges can be minimized by, for example, using a rotary valve to prebulk small volumes of charged powder prior to its collection in a large receiver (Britton, "Static Hazards Using Flexible Intermediate Bulk Containers for Powder Handling," *Process Safety Progress* **12,** no. 4, pp. 240–250, October 1993).

Personnel and Clothing Sparks from ungrounded persons pose a serious ignition hazard in flammable gas-air, vapor-air, and some dust-air mixtures, because the body is a conductor and can store energies on the order of 40 mJ. Induction of charges on a person's ungrounded body by charged clothing is a common cause of personnel electrification. Even at the *threshold of shock sensation,* the stored energy is about 1 mJ.

It is essential that persons be grounded in hazardous (classified) locations. For most chemical operations, the resistance to ground from the body should not exceed 100 megohms. A lower allowable resistance may be specified for locations where the presence of primary explosives, hydrogen-air mixtures, oxygen-enriched mixtures, or certain solid-state devices requires faster charge dissipation.

The combination of conductive flooring *and* conductive footwear is the preferred method of grounding. Untreated concrete flooring with conductive footwear is usually adequate, but its conductivity should be measured (Fowler and Klein, "Static Phenomena and Test Methods for Static Controlled Floors," *EOS/ESD Symposium Proceedings,* pp. 27–38, 1992). Where this method is impractical, personnel grounding devices are available.

In most chemical areas, grounded persons can wear any type of clothing safely. For the unusually sensitive environments listed above, antistatic or conductive clothing should be worn, and persons must be grounded. Removal of outer garments in a flammable location can cause hazardous discharges and should be avoided (NFPA 77, *Static Electricity,* para. 2-2, 1993).

Noncontacting Electrostatic Measurements These measurements are made by instruments that respond to the electric fields at their sensing electrodes. Considerable care must be taken in the interpretation of the measurements. The three general types of devices are described as follows.

Static Locator These meters are the least expensive type. They usually indicate in volts, but should not be used for quantitative evaluations.

Static Voltmeter These instruments are calibrated to indicate the potential (V) on an ungrounded conductor and usually have more than one calibrated meter/surface spacing. They can be used, for example, to indicate the potential on ungrounded persons or equipment. A meter that indicates in volts or kilovolts is *not* an electric field meter.

Electric Field Meter These meters are calibrated to indicate the polarity and magnitude of the electric field (V/m) at the sensor. They should have only *one* calibrated meter/surface spacing and should be

designed to establish a reasonably uniform electric field between the charged surface and the meter. This is needed to ensure that the measured field is approximately equal to the field at the charged surface.

To determine the level of electrification on an *insulating* surface, an electric field meter should always be used. There is a direct relationship between the charge density on the surface of an insulator and the electric field intensity at the surface. Measurements should be made at locations where the insulating surface is several inches away from other insulating or conductive surfaces. The area of the measured surface should be large, compared to the field of view of the meter. In locations where a flammable vapor-air mixture has an MIE greater than 0.2 mJ, field intensities of 500 kV/m or more should be considered unsafe.

HAZARDS OF VACUUM

Nomenclature

F_1	Friction loss in equivalent length, ft
g	Acceleration of gravity, ft/s^2
g_c	Conversion factor, ft·lb$_m$/ft·lb$_f$ s^2
H	Total tank vertical height, ft
h_o	Initial fluid height, ft
h_i	Height between tank base and centerline of pump suction, ft
h_f	Final height of liquid above tank base, ft
NPSH	Net positive suction head, ft
P	Final tank vacuum, in Hg
P_o	Atmospheric pressure, lb$_f$/in^2
ρ	Liquid density, lb$_m$/ft^3
R	Tank radius, ft
V_o	Initial airspace volume, ft^3
V_p	Vapor pressure of tank fluid equivalent, ft
γ	Ratio of molar specific heats, C_p/C_v (about 1.4 for diatomic gases)

Introduction Ask any chemical engineer who has had some plant experience what he or she knows about vacuum and the engineer will probably smile and tell some tale about some piece of equipment that tried to turn itself inside out. Usually no one was hurt, and often there was no massive leakage—but not always!

Causes of Vacuum Hazards The design for the internal pressure condition of vessels is usually straightforward and well understood. The design for external pressures is more difficult. The devious ways in which external pressure can be applied can often be overlooked.

Following are some obvious causes of vacuum collapse:

- Liquid withdrawal by pump or gravity draining
- Removal of gas or vapor by withdrawing with a blower, fan, or jet
- Siphoning of liquids

Less obvious causes include:

- Condensation of vapor
- Cooling of hot gas
- Combination of cooling and condensation of a mixture of gas and condensable vapor

Sometimes obscure causes of vacuum collapse include:

- Absorption of a gas in a liquid, for example, ammonia in water or carbon dioxide in water.
- Reaction of two or more gases to make a liquid or solid, for example, ammonia plus hydrogen bromide to form ammonium bromide.
- Reaction of a gas and a solid to form a solid, for example, corrosion in a tank. Air plus Fe or FeO may give Fe_2O_3 in the presence of water.
- Reaction of a gas and a liquid to give a liquid, for example, chlorination, hydrogenation, or ethylation.
- Sudden dropping of finely divided solids in a silo, creating a momentary vacuum that can suck in the sides of the silo.
- Plugging of flame arresters, for example:

In styrene service, vapor may condense in flame arresters, and the liquid formed is low in inhibitor. Liquid may polymerize and plug off the arrester. Possible solutions include cleaning the arrester frequently or using a PVRV (pressure-vacuum relief valve).

In liquid service in cold weather, vapor may condense in a flame arrester and the liquid formed may freeze and plug the arrester. A possible solution is to heat and insulate the arrester to prevent condensation.

- Maintenance and testing. It is not a good idea to apply vacuum on a vessel during maintenance or testing without full knowledge of the external pressure rating, unless a suitable vacuum relief device is in place and operable.

Location of Vacuum Relief Device (Carl Schiappa, Michigan Engineering, The Dow Chemical Company, Midland, Mich., personal communication, March 20, 1992.) If a vacuum relief device is used, locate the device at the highest point on the top of the tank. If the vacuum relief device is not installed in this location and the tank is overfilled with liquid, the relief device will be sealed in liquid and will be ineffective in protecting the tank. This is especially true for the part of the tank above the vacuum relief device if it is sealed in liquid, the liquid level is lowered, and the tank goes into a partial vacuum.

Protective Measures for Equipment There have been many incidents where vessels were designed for internal pressures of 25 psig or higher and the tank collapsed under vacuum. The internal pressure rating is not a good indication of the vacuum rating. If equipment may be subject to vacuum, consideration should be given to designing the equipment for full vacuum. This may eliminate the need for complicated devices such as relief valves and instruments; if they are used but fail or plug, designing the equipment for full vacuum will prevent collapse of the vessel. For vessels where steam is used in the tank, such as steam-sterilized sanitary-service tanks, a full vacuum rating is advisable under any circumstances.

A disadvantage of this approach is that it may appear at first to be more expensive to design equipment for full vacuum. The cost differential of adding vacuum rating is usually modest compared to the tank's value. It can be less than 10 percent for 15 psig tanks of up to 3000-gal nominal capacity (Wintner, "Check the Vacuum Rating of Your Tanks," *Chem. Eng.,* February 1991, pp. 157–159). When the total cost of a suitably instrumented vessel not designed for vacuum is compared with the cost of a vessel designed for vacuum but without the extra equipment, the difference may be small or negligible, and the vessel designed for vacuum will be inherently safer. If a vessel is designed for vacuum, precautions should be taken to ensure that internal or external corrosion will not destroy the integrity of the vessel. Dimpled jackets may provide an economical way of providing vacuum protection when jacketed vessels are involved.

Personnel Hazards The following case history illustrates how vacuum can be harmful and dangerous to personnel. A plant superintendent was checking an open nozzle on a glass-lined reactor on which there was a vacuum pump pulling vacuum, when suddenly his arm was sucked into the nozzle, up to his shoulder. He could not remove his arm until help arrived to release the vacuum on the vessel. He was injured painfully, though not seriously. The injury could have been very serious if help had not been nearby. Personnel hazards can also result from vacuum conveyor systems for solids handling.

Examples of Vacuum-Related Accidents Figure 26-47 shows a jacketed tank, where the jacket was designed for low-pressure steam. When the steam was turned off and the drain valve and trap were closed, the steam condensed, causing the jacket to collapse. The jacket should have been designed for full vacuum, or a suitable vacuum relief device should have been installed on the jacket.

Figure 26-48 shows the collapse of a large storage tank containing acetone. The overflow and vent line had recently been changed, so it would vent through a vapor seal of water to remove acetone emissions from the vent when the tank was being filled. When the tank was being emptied, water was sucked into the vent pipe, creating a vacuum in the tank, which collapsed the top of the tank. A suitable vacuum relief device on the tank should have been installed to prevent this incident. Venting the tank through a liquid seal of this type is probably not very effective and a better method of controlling emissions should have been selected.

Low-Pressure Storage Tanks Low-pressure storage tanks are fragile. Even an eggshell can withstand more pressure and vacuum (Sanders, "Don't Be Another Victim of Vacuum," *Chemical Eng. Prog.,* September 1993, pp. 54–57). Low-pressure storage tanks do not require much pressure difference between the inside of the tank and the atmosphere to buckle the relatively thin tank walls. Pressure

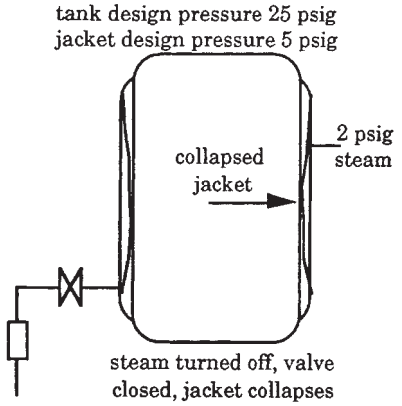


FIG. 26-47 Collapse of vessel jacket due to condensation of steam. (*W. T. Allen, Michigan Engineering, The Dow Chemical Company, Midland, Mich., personal communication, May 1988.*)

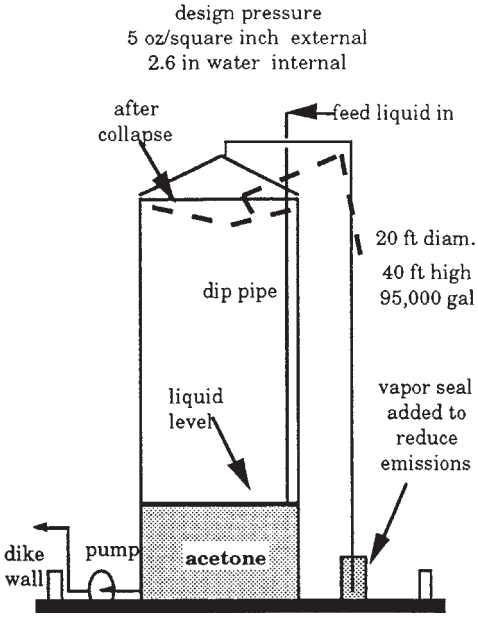


FIG. 26-48 Collapse of storage tank due to adding a liquid vapor seal to reduce vapor emissions. (*Allen, 1988.*)

differences as low as 10 mbar (0.01 atm, or 0.15 psig, or 0.7 in H_2O) between the inside and outside of the tank can buckle some tanks. The rate of handling of product and the breathing volume flow rate due to weather effects must be taken into account in designing the necessary pressure compensation devices.

A critical situation arises in summer when the tank is heated by strong radiation, then cooled by sudden rainfall. Heavy rainfall results in a rapid drop in ambient temperature and the formation of a rainwater film that flows on the top of the tank and down the tank wall. The wall and, with a certain lag, the gas in the tank are cooled, and air must flow into the tank to prevent a significant pressure difference from arising between the inside and outside of the tank. If vapors in the tank are condensed, more air must flow into the tank.

The initial gas temperature in a tank can reach a value of 55°C (131°F) as a result of strong solar radiation. Ambient rainfall is assumed to be 15°C (59°F). The maximum flow rate of air into the tank is reached some minutes later. At the start of the rainfall, after a certain lag, the flow rate at first increases, then reaches a maximum, then decreases.

A study has been made to allow the prediction of the rate at which air must enter a tank with and without internal condensation to prevent a pressure difference from arising (Fullarton, Evripidis, and Schlünder, Institut für Thermische Verfehrenstechnik, Universität Karlsruhe (TH), "Influence of Product Vapour Condensation on Venting of Storage Tanks," *Chem. Eng. Process.*, **22**(3), 1987, published by Elsevier-Sequoia, New York). The results are too involved to be presented in detail here. The reader is referred to this paper for details of the calculations.

The results of a specific case study are shown in Fig. 26-49. This depicts the change in inbreathing volume flow rate as a function of time. The middle curve describes the case when the tank is filled with dry air: that is, no condensation occurs. When the air is saturated with water vapor at 55°C (131°F) and condensation occurs, the top curve is obtained. The bottom line represents the volume flow rate brought about by thermal contraction alone, not including the amount condensed. Because of the heat of condensation released, this fraction is less than the volume flow rate without condensation, but this effect is more than compensated for by the additional volume flow rate due to condensation.

Experimental data in small equipment has shown that condensation of water vapor causes a twofold increase in the maximum flow rate compared to dry air, and a fourfold increase in condensation of methanol vapor.

API 2000 lists the venting capacity for inbreathing (vacuum relief) and outbreathing (pressure relief) for oil tanks up to 180,000 barrels (7,560,000 gal or 2.86×10^4 m^3) capacity at 14.7 psia and 60°F. Tanks larger than 180,000 barrels require individual study (API 2000, "Venting Atmospheric and Low-Pressure Storage Tanks, Non-Refrigerated and Refrigerated," *API Standard 2000*, 3d ed., American Petroleum Institute, Washington D.C., January 1983).

Vacuum Requirements for Draining Tanks (Wintner, 1991, by permission.) A shortcut method of calculating the vacuum that can occur when a tank is being drained while the vent line is closed can be performed by measuring the head in the tank, assuming it is completely full. This is the maximum vacuum that would exist in a gravity-drain tank before air would begin to enter it. If the tank's overall height is designated H, then this vacuum is $2.036H\rho(g/g_cP_o)$ in Hg.

If the tank has some headspace, as is usually the case, it is desirable to get a better estimate of the actual level, since tanks usually have some gas headspace even when filled with liquid. Two tank configurations are considered: the gravity discharge tank (discharge is open to the atmosphere) and the pumped discharge tank. These calculations assume that the process is so rapid that an adiabatic model for the gas in the headspace is the correct choice. This is true when the drainage

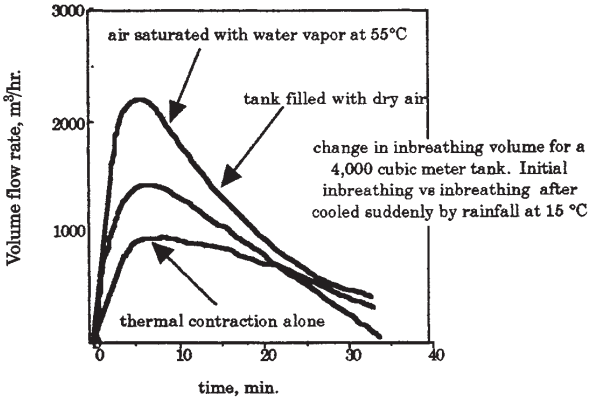


FIG. 26-49 Effect of water vapor condensation on volume flow rate of air into tank. (*Fullarton, Evripidis, and Schlünder, 1987, by permission of Elsevier Science S.A., Lausanne, Switzerland.*)

time is short (on the order of a few minutes for a tank of several thousand gallons capacity). An isothermal model is the best choice when the drain time is long.

For the gravity discharge case, the height of the fluid at maximum vacuum, which is the point at which air would begin to backflow into the tank, is determined by Eq. (26-54). Equation (26-55) calculates the corresponding vacuum in the tank's headspace at this liquid height. Since the drain nozzle is open to the atmosphere, this solution is a static force balance that is satisfied when the sum of the internal pressure and the remaining fluid head is equal to the atmospheric pressure.

$$h_f = \frac{144P_o(1 - \{V_o/[V_o + \pi R^2(h_o - h_f)]\}^\gamma)}{\rho g/g_c} \tag{26-54}$$

$$P = \frac{29.92\, h_f \rho g}{144 P_o g_c} \tag{26-55}$$

$$h_f = \text{NPSH} + F_1 + VP - h_i - \frac{144P_o\,(1 - \{V_o/[V_o + \pi R^2(h_o - h_f)]\}^\gamma)}{\rho g/g_c} \tag{26-56}$$

$$P = 2.036P_o[1 - \{V_o/(V_o + \pi R^2 h_o)\}^\gamma] \tag{26-57}$$

For the pumped-discharge case, internal pressure and final fluid height are calculated by Eqs. (26-56) and (26-57). The final fluid level is the point at which the net positive suction head (NPSH) equation is satisfied.

The solutions of Eqs. (26-54) and (26-56) involve a trial-and-error technique or a numerical method. This can be solved using a computer program for multivariable equations, or it can be calculated by hand. In either equation, assume a reasonable value for h_f and insert it on the right-hand side of the equation. The left-hand value obtained is then substituted until the values guessed at and those calculated are in close agreement. The number of trials is strongly dependent on the initial guess; for realistic tank dimensions, between four and ten iterations should produce good agreement.

The pumped-discharge case is generally more difficult to solve because of the uncertainty in dealing with negative numerical results. As a final answer, a negative value could indicate that the pump has completely emptied the tank; however, as an intermediate value, it could mean that it is not a true solution. A simple check is to try a different initial estimate and see if the intermediate negative results disappear.

Example Assume the tank in Fig. 26-50 has a diameter of 4 ft and a capacity of 1000 gal, is filled with water, and discharges to the atmosphere. The shortcut calculation (tank is initially completely full) indicates that the internal pressure would be 10.65 in Hg. An initial fillage of 70 percent of the tank's volume would produce a vacuum of 6.93 in Hg, which is 65 percent of the shortcut result.

In the case of pumped discharge, assume that a centrifugal pump is used. Its NPSH will determine the height at which vacuum is released by the backflow of air through the pump. Detailed information about the pump characteristics is needed to evaluate the potential vacuum. For these design calculations, assume that the pump will stop delivering liquid and air backflow will begin when the pump's NPSH requirements are no longer met (Sommerfield, "Tank Draining Revisited," *Chem. Eng.,* May 1990, p. 171).

The precise flow-decay pattern will depend on the type, size, and dimensions of the pump. Flow for a typical centrifugal pump will begin to decay at the NPSH point, but some additional fluid transfer will usually occur before a steady backflow of air through the pump begins. At that point, the pump's priming is completely lost.

The mathematical solution for maximum vacuum is based on Eq. (26-56), which solves the NPSH equation for this value of the fluid height. The nomenclature used contains only positive numbers for elevation, with the base point being set at the tank's discharge nozzle (analogous to the gravity-discharge case).

For this example, assume the following parameters:

Pump capacity = 50 gal/min
Pipe = 100 ft of 2-in pipe

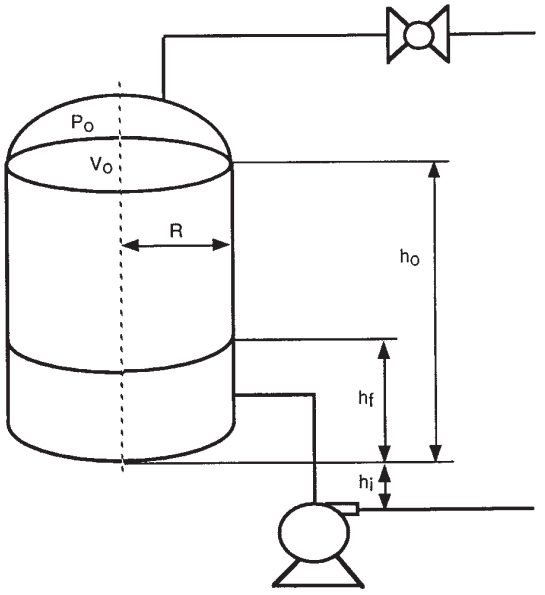


FIG. 26-50 Tank configuration used in example calculation.

NPSH = 4 ft
Elevation H_i = 1 ft
R = 2 ft
Liquid = water at 190°F
P_o = 14.7 psia

For these parameters, the equations predict a much higher vacuum (24.5 in Hg or 230 percent of the shortcut method) than the gravity-discharge case. Of course, different tank dimensions and pump characteristics could give different comparisons between cases. If conditions are such that the pump can completely empty the tank before backflow occurs, the vacuum is best calculated from Eq. (26-57).

If proper instruments are provided, the tank and pump can be interlocked, so the pump will stop when abnormal conditions are detected. This may help keep the tank from collapsing, but the gravity-discharge case should also be checked to ensure that failure will not occur after the interlock stops the pump. In all cases where instrumentation is used, the consequences of potential failure should be considered.

HAZARDS OF INERT GASES

GENERAL REFERENCES: Air Products and Chemicals Co., *Dangers of Oxygen Deficient Atmospheres,* Allentown, Pa., 1988. ASHRAE Standard 34, "Fluorocarbon Numbering for Methane, Ethane and Cycloalkane Refrigerants," 1978. ASHRAE Standard 62-1989, American Society of Heating Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Ga., 1989. Bartknecht, *Dust Explosions,* Springer-Verlag, Berlin, 1989. Bartknecht, *Explosion Course Prevention, Protection,* Springer-Verlag, Berlin, 1981. Bodurtha, *Industrial Explosion Prevention and Protection,* McGraw-Hill, 1980. Generon Systems (membrane systems for producing moderate- to high-purity nitrogen), 400 W. Sam Houston Parkway South, Houston, Tex., 1993. *Guidelines for Engineering Design for Process Safety,* CCPS-AIChE, New York, 1993. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980. Nagy, Dorsett, and Jacobson, "Preventing Ignition of Dust Dispersions by Inerting," *U.S. Bur. Mines Rep. Invest. 6543,* 1964. NFPA 68, *Venting of Deflagrations,* National Fire Protection Association, Quincy, Mass., 1988. NFPA 69, *Explosion Prevention Systems,* National Fire Protection Association, Quincy, Mass., 1992. NFPA 654, *Standard for Fire and Dust Explosion Prevention in the Chemical, Dye, Pharmaceutical and Plastics Industries,* National Fire Protection Association, Quincy, Mass. 1982. Niida et al., *Some Expert System Experiments in Process Engineering,* Chem. Eng. Res. Des., vol. 64, September 1986, p. 374. *Ventilation for Acceptable Indoor Air Quality,* American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Ga. Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors,* Bulletin 627, Bureau of Mines, 1965.

Introduction The use of inert atmospheres should be considered to prevent fires and deflagrations when using flammable materials. However, inert atmospheres can be dangerous to personnel. One of the most important concerns in the use of an inert atmosphere is that it can kill if a person breathes it. The air we normally inhale contains about 21 percent O_2, 79 percent N_2, and small amounts of other components. Inhaling air containing less than about 16 percent oxygen causes dizziness, rapid heartbeat, and headache. One or two breaths of pure nitrogen and some other gases containing no oxygen can be lethal. Other gases of this type include methane, ethane, acetylene, carbon dioxide, nitrous oxide, hydrogen, argon, neon, helium, and some others. Oxygen in the lungs is washed out and replaced by gas containing no oxygen. Blood from the lungs receives insufficient oxygen and flows to the brain, where tissues rapidly become deficient. Within five seconds of inhaling only a few breaths of oxygen-free gas, there can be mental failure and coma. Symptoms or warnings are generally absent. Death follows in two to four minutes. However, a coma due to lack of oxygen is not always fatal. Cardiopulmonary resuscitation techniques should be used on persons who are not breathing due to lack of oxygen (*Ventilation for Acceptable Indoor Air Quality,* American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Ga.; Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors,* Bulletin 627, Bureau of Mines, 1965).

Gases which act as simple asphyxiants, such as nitrogen and helium, merely displace oxygen in the atmosphere so that the concentration falls below that needed to maintain consciousness. There are also chemical asphyxiants, such as carbon monoxide, hydrogen sulfide, and hydrogen cyanide, which have a specific blocking action and prevent a sufficient supply of oxygen from reaching the body. Most deaths due to short-term gassing are caused by carbon monoxide (Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980, p. 646).

Effects of Low Oxygen Levels There are many factors which can affect the ability of human beings to adjust to lower oxygen levels. For example, two men were accidentally exposed to a low oxygen level in a vessel. One of them died, and one survived without permanent injury. The one who died had been in poorer general health and it is believed that this factor may have made the low oxygen level fatal for him, while the other person, who was in good health, survived.

It is well known that people accustomed to living near sea level can take several days to adjust fully to the lower amount of oxygen available in mountainous regions such as Denver, Colorado. Anyone who has traveled to the top of Pike's Peak knows how the altitude can make one tired, lethargic, and even sick. People react differently, however, and one cannot generalize as to exactly how a person will react to lower oxygen levels and higher altitudes. Table 26-25 gives the signs and symptoms of reduced oxygen content on persons at rest.

Minimum Oxygen Limits Oxygen limits are set at 19.5 percent minimum as recommended by OSHA and the American Standards Institute. Michigan has adopted these guidelines as well and has defined grade D air for O_2 to be 19.5 percent to 23.5 percent as an obligation to the employee by their employer. The Ontario Ministry of Labour designates enclosures containing less than 18 percent O_2 as hazardous.

Confined-Space Entry by the Dow Chemical Company The Dow Chemical Company Safety Standard on Confined-Space Entry states the following regarding confined space entry.

1. Check all test instruments to assure they are operable before and after use.
2. Readings acceptable for entry shall be recorded on the Safe Work Permit and shall assure that the oxygen content is 21 percent plus or minus 0.5 percent.
3. Toxic materials shall be at or below the threshold limit value, permissible exposure limit, or other approved industrial hygiene guideline.
4. The combustible gas indicator must be calibrated using the appropriate calibrating gas, such as methane or pentane.
5. The analysis shall be in the following sequence: oxygen concentration, then the combustible gas or vapor.

Confined-Space Entry as Defined by OSHA (Taylor, Shoemaker, and Sasse, "Confined Space Entry," *AIChE 1990 Summer National Meeting,* San Diego, Calif., August 19–22, 1990.) Occupational Safety and Health Administration (OSHA), in Section 1926.21(b)(6)(ii), has defined confined space as space having a limited means of egress, which is subject to the accumulation of toxic or flammable contaminants or has an oxygen-deficient atmosphere. For the purpose of this section, confined-space entry is discussed only as it pertains to process vessels, catalytic reactors, and storage tanks. OSHA classifies confined-space entry into two categories: immediately dangerous to life and health (IDLH) and non-IDLH as follows:

Class A—immediately dangerous to life and health based on oxygen level less than 19.5 percent and/or airborne presence of toxic or poisonous substances in concentration constituting IDLH conditions; flammability up to 20 percent of lower flammable limit.

Class B—Non-IDLH based on oxygen level between 19.5 and 21 percent, but classified as dangerous due to the airborne presence of toxic or poisonous substance below IDLH level, but greater than the protection factor offered by air-purifying respirators.

In addition, there is a non-IDLH class based on oxygen level between 19.5 and 21 percent, but classified as hazardous due to the presence of nuisance dusts or vapors below the IDLH level, but not greater than the protection factor of air-purifying respirators or low concentration of toxic or flammable substances.

Case Histories Following are examples of fatal accidents resulting from lack of oxygen:

- In a chemical plant, compressed nitrogen was temporarily being used to supply a control room, which was usually closed, containing pneumatic process control instruments that normally used instrument air. With the normal venting of nitrogen by the instruments in the control room, the air in the room was gradually replaced. An instrument man entered the control room for maintenance and was overcome by the lack of oxygen and died.
- Two men were inspecting a large tank in which other equipment was installed. The tank had two large manways attached to it, one near the bottom and one near the top. Ventilation was provided by air entering the bottom manway and leaving the top manway. A sheet of plastic had temporarily been placed over the top manway, which decreased the amount of air circulation. One of the inspectors climbed a ladder in the tank, became dizzy, and fell to the tank floor below. He died from the injuries received in the fall. It was found that

TABLE 26-25 Effects of Breathing Oxygen-Deficient Atmospheres

Oxygen content of air, %	Signs and symptoms of persons at rest
19.5–23.5	Recommended by OSHA.
15–19	Decreased ability to work strenuously. May impair coordination and may induce early symptoms in persons with coronary, pulmonary, or circulatory problems.
12–17	Loss of balance, dizziness. Respiration deeper, increased pulse rate, impaired coordination, perception, and judgment.
10–12	Further increase in rate and depth of respiration, further increase in pulse rate, performance failure, giddiness, poor judgment, lips blue, prolonged exposure possibly results in brain damage.
8–10	Mental failure, nausea, vomiting, fainting, unconsciousness, ashen face, blueness of lips. 8 minutes: 100% fatal. 6 minutes: 50% fatal. 4 to 5 minutes: recovery with treatment; brain damage and death are possible.
4	Coma in 40 s, convulsions, respiration ceases, death.

SOURCE: Air Products and Chemicals Co., "Dangers of Oxygen Deficient Atmospheres," Allentown, Pa., 1988, and American Standards Institute, Report No. 788.

the oxygen level in the upper part of the tank was 12.3 percent, which was low enough to cause dizziness and loss of balance. When the plastic sheet was removed, the oxygen content quickly rose to 21 percent. It was concluded that steel inside the tank had corroded, causing low oxygen content in the tank. Impaired ventilation caused by the plastic sheet had reduced circulation so that the air in the upper part of the tank remained at a low oxygen concentration.

Inerting Monomer Storage Tanks with Nitrogen It is good practice to keep the vapor space of flammable liquids out of the flammable range. Monomers that can potentially polymerize require special consideration. The vapor space above some monomers, such as styrene and methyl acrylate, should be kept below about 10 percent oxygen in warm weather to be below the flammable range. For many of these monomers, a small amount of oxygen is required to maintain the activity of the inhibitor and to avoid polymerization in storage tanks, which could lead to overheating and explosions and fire. An oxygen concentration of 5 percent in the vapor space is recommended as a safety factor to stay out of the flammable range and maintain inhibitor activity.

Maintaining an inert atmosphere for these applications can be difficult, since usually nitrogen is available as a high-purity gas, and it is necessary to add a small amount of oxygen (usually air) to the nitrogen to achieve the desired oxygen concentration. Mixing air and nitrogen has not proven to be a reliable method of maintaining the proper inert pad in the past. This is because instrument failure has caused high nitrogen concentration, which in turn has caused storage vessels to polymerize. One alternative to consider is the use of membrane systems, such as those sold by Generon Systems and other suppliers. This system can produce 95/5 percent nitrogen/oxygen for inerting, using plant compressed air available at 65 psig (449 kPa gauge). This system has an inherently stable output when operating at a specific pressure drop because the pressure drop across the membrane module sets the nitrogen purity.

Halon Systems for Inerting The term *halon* is generic for a range of halogenated hydrocarbons in which one or more of the hydrogen atoms have been replaced by atoms from the halogen series. Fully halogenated hydrocarbons are considered *hard* halons because it is believed that they have a major effect on the ozone layer. They work as fire-extinguishing agents by interfering with the free radical chain reaction occurring in flames. However, they destroy ozone in the same way. Halons containing bromine are much more destructive of ozone than chlorofluorocarbons (CFCs). It has been reported that one atom of some halons can destroy 10^6 ozone molecules. Halon alternatives that have less effect on the ozone layer include HCFCs, which are halogenated hydrocarbons with at least one hydrogen atom. In 1987, the Montreal Protocol on Protection of the Stratospheric Ozone Layer was signed, which set a timetable for phasing out the production and use of CFCs, including halons. The date for phaseout of the manufacture of halons according to the latest Copenhagen Meeting was January 1, 1994 (UNEP, Montreal Protocol on Substances that Deplete the Ozone Layer—Final Act 1987, 1987).

Although there have been many materials under development to replace the halons, there is not a single material that is a drop-in replacement. Some HCFCs are low in ozone depletion allowance, compared to halons or other CFCs, but in the long term, the goal should be zero ozone depletion. It is probable that there are no absolutely essential applications for halon in the chemical industry. There may be essential uses in airplanes, submarines, etc. Suggested replacements are water, dry chemical, and carbon dioxide. A large use for halon systems is in the form of total halon flooding systems for computer centers. To reduce the need for halon systems for computer centers, modern computer centers have a minimum amount of combustible materials to cause heat generation and there is less cable insulation with the use of fiber optics. Smoke and heat detectors are first-line-of-defense measures, along with emergency electrical power shutoff switches.

Fine water spray systems may be potentially superior to CO_2 applications and may replace halon environments such as telephone central offices and computer rooms. In the fine spray delivery system, water is delivered at relatively high pressure (above 100 psi [0.689 MPa]) or by air atomization to generate droplets significantly smaller than those generated by sprinklers. Water flow from a fine spray nozzle potentially extinguishes the fire faster than a sprinkler because the droplets are smaller and vaporize more quickly. Preliminary information indicates that the smaller the droplet size, the lower the water flow requirements and the less chance of water damage.

Inert Gas Generation Nitrogen is often the preferred gas for providing an inert atmosphere. In general, most organic combustible compounds will not propagate flame if oxygen in the mixtures of the organic vapor, inert gas, and air is below about 10 percent and 13 percent, with nitrogen and carbon dioxide, respectively, as the inert gases. With carbon dioxide, the minimum oxygen concentration is higher than with nitrogen because carbon dioxide has a higher specific heat. Carbon dioxide is fairly soluble in many liquids and will react with alkaline materials, so its use as an inerting material is limited. Heavy gases such as carbon dioxide provide superior inerting of vent stacks to prevent air entry. Water vapor is a good inerting gas if the temperature is high enough (above about 80 to 85°C [176 to 185°F]). Water vapor has a higher specific heat than nitrogen, so less water vapor is required for inerting than nitrogen (*FMRC Update,* vol. 7, no. 3, Factory Mutual Engineering Corp., Norwood, Mass., December 1993, pp. 2, 3).

Table 26-26 lists some of the main commercial methods used to generate nitrogen or nitrogen-rich gas.

TABLE 26-26 Commercial Methods Used to Generate Nitrogen or Nitrogen-Rich Gas

Process	Purity	Capacity	Features
Cryogenic separation	Very high N_2 purity, 99.999%, by-products oxygen and argon	Can be high	Very high purity; high flexibility by storing liquid nitrogen; fairly high capital costs, modest operating costs; complicated process
Pressure swing adsorption using molecular sieves	High purity, 99 to 99.9% N_2	Moderate	High purity; high-pressure storage may be required; simple process; economical
Membrane separation	Medium to high purity N_2, 95 to 99.9%	Small; typical module produces 855 scfh at 175 lb/in^2 and 77°F	Can use plant air as air source; simple and safe to operate; stable output; may be economical for low-capacity, medium- to high-purity requirements; excellent when some oxygen is required with the nitrogen; temperature and pressure sensitive
Hydrocarbon combustion	Contaminated with other gases: N_2 ~ 85% CO_2 ~ 14% CO ~ 0.5% O_2 ~ 0.5% H_2O ~ saturated	Small	Simple process; can use combustion products from engines or boilers, or dedicated burner; less reliability of O_2 control; may be very economical; used on tanker ships
Ammonia decomposition	Contaminated with H_2, water; N_2 ~ 75–99.5%, very low O_2	Small	Used only when cheap NH_3 is available

SOURCE: K. Niida, et al., Some Expert System Experiments in Process Engineering, *Chem. Eng. Res. Des,* vol. 64, September 1986, p. 374; Generon Systems, 400 W. Sam Houston Parkway South, Houston, Tex., 1993.

Conclusions The use of an inert atmosphere can virtually eliminate the possibility of explosions and fire with flammable materials. However, inerting systems can be quite expensive and difficult to operate successfully and can be hazardous to personnel. Before using inert systems, alternatives should be explored, such as using nonflammable materials or operating below the flammable range.

GAS DISPERSION

Nomenclature

A	Area affected by release, length^2
A°	Dimensionless impact area
C	Concentration, mass/volume
$\langle C \rangle$	Time-averaged concentration, mass/volume
$\langle C \rangle^\circ$	Concentration of interest, mass/volume
D_c	Characteristic source dimension for continuous releases of dense gases, defined by Eq. (26-72), length
D_i	Characteristic source dimension for instantaneous releases of dense gases, defined by Eq. (26-73), length
g	Acceleration due to gravity, length/time^2
g_o	Initial buoyancy factor, defined by Eq. (26-71), length/time^2
H_r	Height of release above ground level, length
K	Eddy diffusivity, area/time
L°	Scaled length, defined by Eq. (26-66), length
M	Molecular weight, mass/mole
P	Pressure, force/area
q_o	Initial plume volume flux for dense gas dispersion, volume/time
Q_m	Continuous release rate of material, mass/time
Q_m°	Instantaneous release of material, mass
R_d	Release duration, time
T	Absolute temperature, K
t	Time, s
u	Wind speed, length/time
V_o	Initial volume of released dense gas material, length^3
x,y,z	Distance in dimensional space, length
x_v,y_v,z_v	Virtual distances for plume, length
x°	Dimensionless downwind distance
	Greek symbols
$\sigma_x,\sigma_y,\sigma_z$	Dispersion coefficients, length
ρ_a	Density of ambient air, mass/volume
ρ_o	Initial density of released material, mass/volume
	Subscripts
a	Ambient
j	Either x, y, or z length dimensions
o	Initial
v	Virtual
	Superscripts
$'$	Stochastic or fluctuating quantity

General References: Crowl and Louvar, *Chemical Process Safety: Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, NJ, 1990, pp. 121–155. Hanna and Drivas, *Guidelines for Use of Vapor Cloud Dispersion Models,* AIChE, New York, 1987. Hanna and Strimaitis, *Workbook of Test Cases for Vapor Cloud Source Dispersion Models,* AIChE, New York, 1989. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1986, pp. 428–463. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution,* Chaps. 12, 13, 14, Wiley, New York, 1986. Turner, *Workbook of Atmospheric Dispersion Estimates,* U.S. Department of Health, Education, and Welfare, Cincinnati, 1970.

Introduction Gas dispersion (or vapor dispersion) is used to determine the consequences of a release of a toxic or flammable material. Typically, the calculations provide an estimate of the area affected and the average vapor concentrations expected. In order to make this determination, one must know the release rate of the gas (or the total quantity released) and the atmospheric conditions (wind speed, time of day, cloud cover).

The steps required to utilize a gas dispersion model are:

1. Identify the scenario. What can go wrong to result in the loss of containment of the material?
2. Develop an appropriate source model to calculate the release rate or total quantity released based on the specified scenario (see Discharge Rates from Punctured Lines and Vessels).
3. Use an appropriate gas dispersion model to estimate the consequences.
4. Determine if the resulting consequence is acceptable. If not, then something must be changed to reduce the consequence.

The entire procedure is shown in Fig. 26-51. If the consequence is not acceptable, then some of the options available to reduce the consequence are shown in Table 26-27.

Calculations and experiments have demonstrated that even the release of a small quantity of toxic or flammable material can have a significant consequence. Thus, it is clear that the best procedure is to prevent the release in the first place. However, release mitigation must be a part of any process safety program. Release mitigation involves: (1) detecting the release as early as possible, (2) stopping the release as quickly as possible, and (3) invoking a mitigation/emergency response procedure to reduce the consequences of the release.

Parameters Affecting Gas Dispersion A wide variety of parameters affect the dispersion of gases. These include: (1) wind speed, (2) atmospheric stability, (3) local terrain characteristics, (4) height of the release above the ground, (5) release geometry, i.e. from a point, line, or area source, (6) momentum of the material released, and (7) buoyancy of the material released.

As the wind speed is increased, the material is carried downwind faster, but the material is also diluted faster by a larger quantity of air.

Atmospheric stability depends on the wind speed, the time of day, and the solar energy input. During the day, the air temperature is at a maximum at the ground surface as a result of radiative heating of the ground from the sun. At night, radiative cooling of the ground occurs, resulting in an air temperature which is low at ground level, increases with height until a maximum is reached, and then decreases with further height.

Terrain characteristics affect the mechanical mixing of the air as it flows over the ground. Thus, the dispersion over a lake is different from the dispersion over a forest or a city of tall buildings.

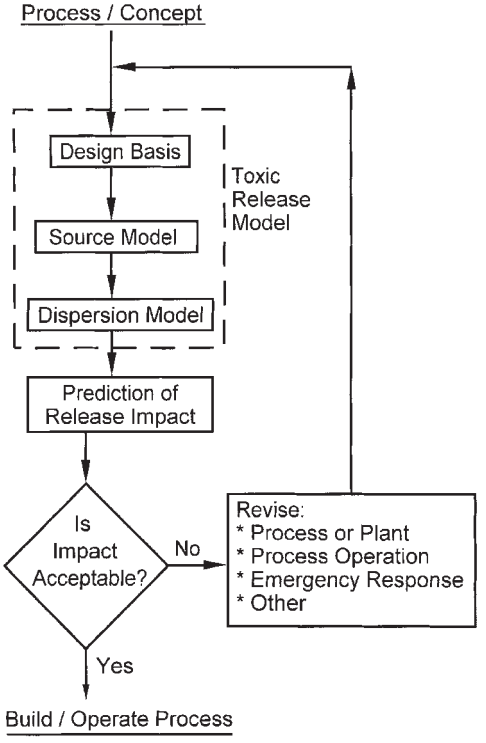


FIG. 26-51 The procedure for using a gas dispersion model to estimate the release impact.

TABLE 26-27 Release Mitigation Approaches

Major area	Examples
Inherent safety	*Inventory reduction:* Fewer chemicals inventoried or fewer in process vessels. *Chemical substitution:* Substitute a less hazardous chemical for one more hazardous. *Process attenuation:* Use lower temperatures and pressures.
Engineering design	*Plant physical integrity:* Use better seals or materials of construction. *Process integrity:* Ensure proper operating conditions and material purity. *Process design features for emergency control:* Emergency relief systems. *Spill containment:* Dikes and spill vessels.
Management	Operating policies and procedures Training for vapor release prevention and control Audits and inspections Equipment testing Maintenance program Management of modifications and changes to prevent new hazards Security
Early vapor detection and warning	Detection by sensors Detection by personnel
Countermeasures	Water sprays Water curtains Steam curtains Air curtains Deliberate ignition of explosive cloud Dilution Foams
Emergency response	On-site communications Emergency shutdown equipment and procedures Site evacuation Safe havens Personal protective equipment Medical treatment On-site emergency plans, procedures, training, and drills

SOURCE: Adapted from Prugh and Johnson, *Guidelines for Vapor Release Mitigation,* AIChE, New York, 1988.

Figure 26-52 shows the effect of height on the downwind concentrations due to a release. As the release height increases, the ground concentration downwind decreases since the resulting plume has more distance to mix with fresh air prior to contacting the ground.

The geometry of the release also affects the resulting consequence. An ideal release would occur at a point source. Real releases are more likely to occur as a line source (from an escaping jet of material) or as an area source (from a boiling pool of liquid).

Figure 26-53 shows the affect of initial momentum and buoyancy of the release. If the material is released as a jet, then the effective height of the release is increased. Furthermore, if the material released is heavier than air (which is the usual case for the release of most hydrocarbons), the plume initially slumps toward the ground until subsequent dilution by air results in a neutrally buoyant cloud.

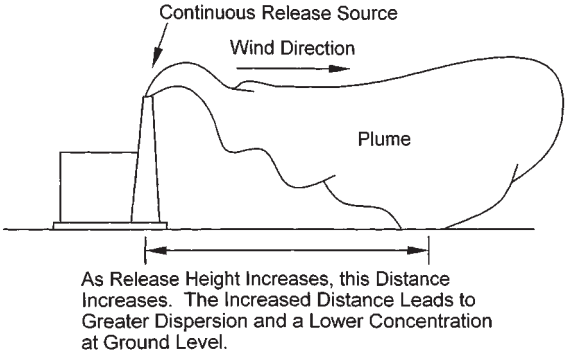


FIG. 26-52 Effect of increased release height on the downwind ground-level concentration. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 127. Used by permission of Prentice Hall.*)

Gaussian Dispersion Gaussian dispersion is the most common method for estimating dispersion due to a release of vapor. The method applies only for neutrally buoyant clouds and provides an estimate of average downwind vapor concentrations. Since the concentrations predicted are time averages, it must be considered that local concentrations might be greater than this average; this result is important when estimating dispersion of highly toxic materials where local concentration fluctuations might have a significant impact on the consequences.

Fundamental Equations A complete development of the fundamental equations is presented elsewhere (Crowl and Louvar, 1990, pp. 129–144). The model begins by writing an equation for the conservation of mass of the dispersing material:

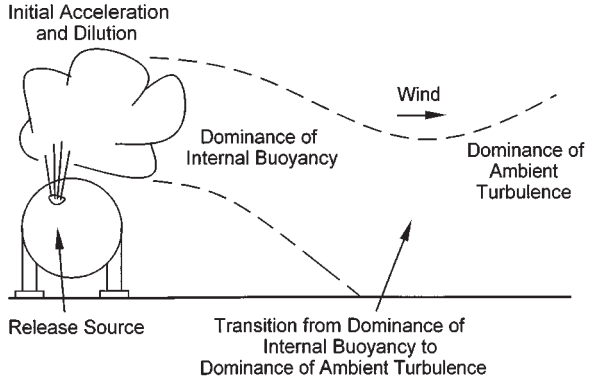


FIG. 26-53 Effect of initial acceleration and buoyancy on the release of gases. (*Adapted from S. R. Hanna and P. J. Drivas,* Guidelines for Use of Vapor Cloud Dispersion Models, *1987. Used by permission of the American Institute of Chemical Engineers, Center for Chemical Process Safety.*)

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x_j}(u_j C) = 0 \qquad (26\text{-}58)$$

where C is the concentration of dispersing material; j represents the summation over all three coordinates, x, y, and z; and u is the velocity of the air.

The difficulty with Eq. (26-58) is that it is impossible to determine the velocity u at every point, since an adequate turbulence model does not currently exist. The solution is to rewrite the concentration and velocity in terms of an average and stochastic quantity: $C = \langle C\rangle + C'$; $u_j = \langle u_j\rangle + u_j'$, where the brackets denote the average value and the prime denotes the stochastic, or deviation variable. It is also helpful to define an eddy diffusivity K_j (with units of area/time) as

$$-K_j \frac{\partial\langle C\rangle}{\partial x_j} = \langle u_j' C'\rangle \qquad (26\text{-}59)$$

By substituting the stochastic equations into Eq. (26-58), taking an average, and then using Eq. (26-59), the following result is obtained:

$$\frac{\partial\langle C\rangle}{\partial t} + \langle u_j\rangle \frac{\partial\langle C\rangle}{\partial x_j} = \frac{\partial}{\partial x_j}\left(K_j \frac{\partial\langle C\rangle}{\partial x_j}\right) \qquad (26\text{-}60)$$

The problem with Eq. (26-60) is that the eddy diffusivity changes with position, time, wind velocity, and prevailing atmospheric conditions, to name a few, and must be specified prior to a solution to the equation. This approach, while important theoretically, does not provide a practical framework for the solution of vapor dispersion problems.

Sutton (*Micrometeorology,* McGraw-Hill, 1953, p. 286) developed a solution to the above difficulty by defining dispersion coefficients, σ_x, σ_y, and σ_z, defined as the standard deviation of the concentrations in the downwind, crosswind, and vertical (x, y, z) directions, respectively. The dispersion coefficients are a function of atmospheric conditions and the distance downwind from the release. The atmospheric conditions are classified into six stability classes (A through F) for continuous releases and three stability classes (unstable, neutral, and stable) for instantaneous releases. The stability classes depend on wind speed and the amount of sunlight, as shown in Table 26-28.

Pasquill (*Atmospheric Diffusion,* Van Nostrand, 1962) recast Eq. (26-60) in terms of the dispersion coefficients and developed a number of useful solutions based on either continuous (plume) or instantaneous (puff) releases. Gifford (*Nuclear Safety,* vol. 2, no. 4, 1961, p. 47) developed a set of correlations for the dispersion coefficients based on available data (see Table 26-29 and Figs. 26-54 to 26-57). The resulting model has become known as the *Pasquill-Gifford model.*

The *puff model* describes near-instantaneous releases of material. The solution depends on the total quantity of material released, the atmospheric conditions, the height of the release above ground, and the distance from the release. The equation for the average concentration for this case is (Crowl and Louvar, 1990, p. 143):

$$\langle C\rangle(x,y,z,t) = \frac{Q_m^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \times \left\{\exp\left[-\frac{1}{2}\left(\frac{z-H_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+H_r}{\sigma_z}\right)^2\right]\right\} \qquad (26\text{-}61)$$

TABLE 26-28 Atmospheric Stability Classes for Use with the Pasquill-Gifford Dispersion Model

Wind speed, m/s	Day radiation intensity			Night cloud cover	
	Strong	Medium	Slight	Cloudy	Calm and Clear
<2	A	A–B	B		
2–3	A–B	B	C	E	F
3–5	B	B–C	C	D	E
5–6	C	C–D	D	D	D
>6	C	D	D	D	D

Stability classes for puff model:
A, B: unstable
C, D: neutral
E, F: stable

TABLE 26-29 Equations and Data for Pasquill-Gifford Dispersion Coefficients

Equations for continuous plumes

Stability class	σ_y, m
A	$\sigma_y = 0.493x^{0.88}$
B	$\sigma_y = 0.337x^{0.88}$
C	$\sigma_y = 0.195x^{0.90}$
D	$\sigma_y = 0.128x^{0.90}$
E	$\sigma_y = 0.091x^{0.91}$
F	$\sigma_y = 0.067x^{0.90}$

Stability class	x, m	σ_z, m
A	100–300	$\sigma_z = 0.087x^{1.10}$
	300–3000	$\log_{10}\sigma_z = -1.67 + 0.902\log_{10}x + 0.181(\log_{10}x)^2$
B	100–500	$\sigma_z = 0.135x^{0.95}$
	500–2×10^4	$\log_{10}\sigma_z = -1.25 + 1.09\log_{10}x + 0.0018(\log_{10}x)^2$
C	100–10^5	$\sigma_z = 0.112x^{0.91}$
D	100–500	$\sigma_z = 0.093x^{0.85}$
	500–10^5	$\log_{10}\sigma_z = -1.22 + 1.08\log_{10}x - 0.061(\log_{10}x)^2$
E	100–500	$\sigma_z = 0.082x^{0.82}$
	500–10^5	$\log_{10}\sigma_z = -1.19 + 1.04\log_{10}x - 0.070(\log_{10}x)^2$
F	100–500	$\sigma_z = 0.057x^{0.80}$
	500–10^5	$\log_{10}\sigma_z = -1.91 + 1.37\log_{10}x - 0.119(\log_{10}x)^2$

Data for puff releases

Stability condition	x = 100 m		x = 4000 m	
	σ_y, m	σ_z, m	σ_y, m	σ_z, m
Unstable	10	15	300	220
Neutral	4	3.8	120	50
Very stable	1.3	0.75	35	7

SOURCE: Frank P. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1986, p. 443).

The center of the puff is located at $x = ut$. Here x is the downwind direction, y is the crosswind direction, and z is the height above ground level. The initial release occurs at a height H_r above the ground point at $(x,y,z) = (0,0,0)$, and the center of the coordinate system remains at the center of the puff as it moves downwind.

Notice that the wind speed does not appear explicitly in Eq. (26-61). It is implicit through the dispersion coefficients since these are a function of distance downwind from the initial release and the atmospheric stability conditions.

A typical requirement is to determine the cloud boundary at a fixed concentration. These boundaries, or lines, are called *isopleths.* The

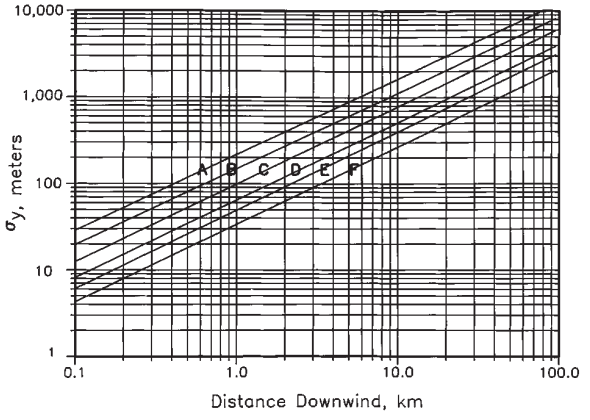


FIG. 26-54 Horizontal dispersion coefficient for Pasquill-Gifford plume model. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 138. Used by permission of Prentice Hall.*)

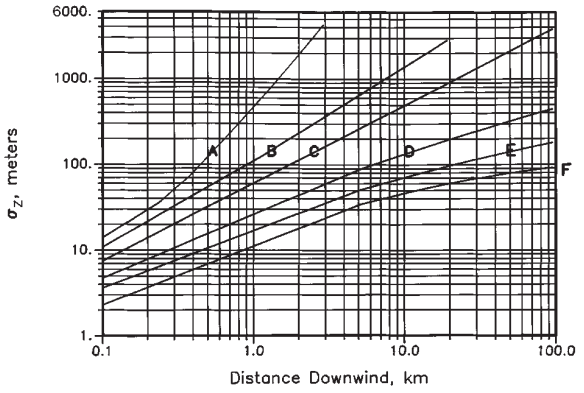


FIG. 26-55 Vertical dispersion coefficient for Pasquill-Gifford plume model. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 138. Used by permission of Prentice Hall.*)

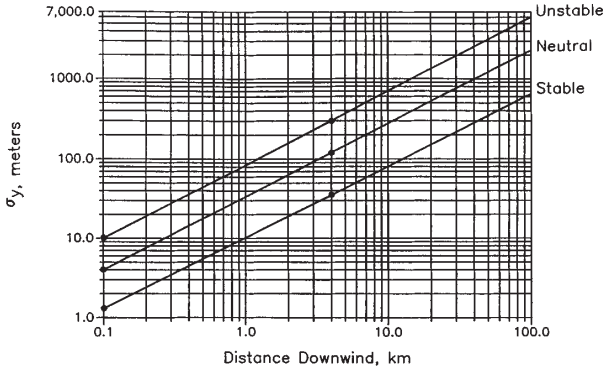


FIG. 26-56 Horizontal dispersion coefficient for Pasquill-Gifford puff model. These data are based on only the data points shown and should not be considered reliable elsewhere. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 140. Used by permission of Prentice Hall.*)

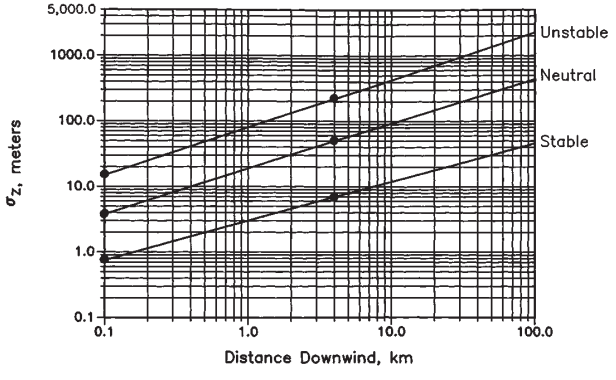


FIG. 26-57 Vertical dispersion coefficient for Pasquill-Gifford puff model. These data are based only on the data points shown and should not be considered reliable elsewhere. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 140. Used by permission of Prentice Hall.*)

locations of these are found by dividing the equation for the centerline concentration, i.e., $\langle C\rangle(x,0,0,t)$, by the general ground-level concentration provided by Eq. (26-61). The resulting equation is solved for y to give

$$y = \sigma_y \sqrt{2 \ln \left(\frac{\langle C\rangle(x,0,0,t)}{\langle C\rangle(x,y,0,t)} \right)} \tag{26-62}$$

The procedure to determine an isopleth at any specified time is:

1. Specify a concentration $\langle C\rangle^*$ for the isopleth.
2. Determine the concentrations $\langle C\rangle(x,0,0,t)$, along the x axis directly downwind from the release. Define the boundary of the cloud along this axis.
3. Set $\langle C\rangle(x,y,0,t) = \langle C\rangle^*$ in Eq. (26-62) and determine the value of y at each centerline point determined in step 2. Plot the y values to define the isopleth, using symmetry around the centerline.

The *plume model* describes continuous release of material. The solution depends on the rate of release, the atmospheric conditions, the height of the release above ground, and the distance from the release. In this case, the wind is moving at a constant speed u in the x direction. The equation for the average concentration for this case is (Crowl and Louvar, 1990, p. 142):

$$\langle C\rangle(x,y,z) = \frac{Q_m}{2\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y} \right)^2 \right] \times \left\{ \exp\left[-\frac{1}{2}\left(\frac{z-H_r}{\sigma_z} \right)^2 \right] + \exp\left[-\frac{1}{2}\left(\frac{z+H_r}{\sigma_z} \right)^2 \right] \right\} \tag{26-63}$$

For releases at ground level, the maximum concentration occurs at the release point. For releases above ground level, the maximum ground concentration occurs downwind along the centerline. The location of the maximum is found using

$$\sigma_z = \frac{H_r}{\sqrt{2}} \tag{26-64}$$

and the maximum concentration is found from

$$\langle C\rangle_{\max} = \frac{2Q_m}{e\pi u H_r^2}\left(\frac{\sigma_z}{\sigma_y} \right) \tag{26-65}$$

The procedure for finding the maximum concentration and the downwind distance for the maximum is to

1. Use Eq. (26-64) to determine the dispersion coefficient σ_z at the maximum.
2. Use Fig. 26-56 to determine the downwind location of the maximum.
3. Use Eq. (26-65) to determine the maximum concentration.

Nomograph Method By defining a scaled length

$$L^* = \left(\frac{Q_m}{u\langle C\rangle^*} \right)^{1/2} \tag{26-66}$$

a dimensionless downwind distance

$$x^* = \frac{x}{L^*} \tag{26-67}$$

and a dimensionless area

$$A^* = \frac{A}{(L^*)^2} \tag{26-68}$$

nomographs can be developed for determining the downwind distance and the total area affected at the concentration of interest $\langle C\rangle^*$. These nomographs are shown in Figs. 26-58 and 26-59.

Virtual Sources The previous equations apply to point source releases. Real releases, such as a boiling pool of liquid or a streaming jet of flashing liquid, involve a more complex geometry. One approach (*Guidelines for Chemical Process Quantitative Risk Analysis,* AIChE, 1989, p. 87) is to define a virtual source upwind from the actual source such that the computed plume matches the real plume. However, to achieve this, a concentration at a centerline point directly downwind must be known.

There are several ways to determine the location of the virtual source for a plume:

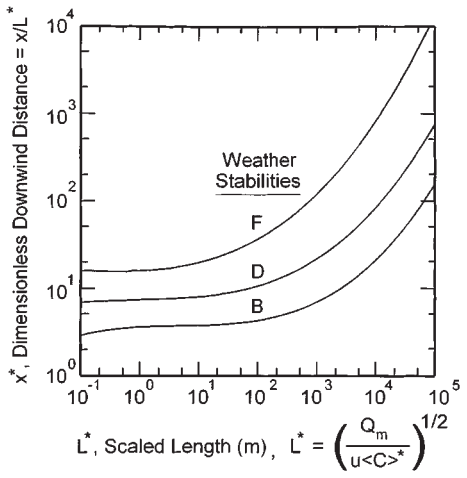


FIG. 26-58 Nomograph to determine the downwind distance affected by a release. (*Adapted from* Guidelines for Chemical Process Quantitative Risk Analysis, *1989, p. 90. Used by permission of the American Institute of Chemical Engineers.*)

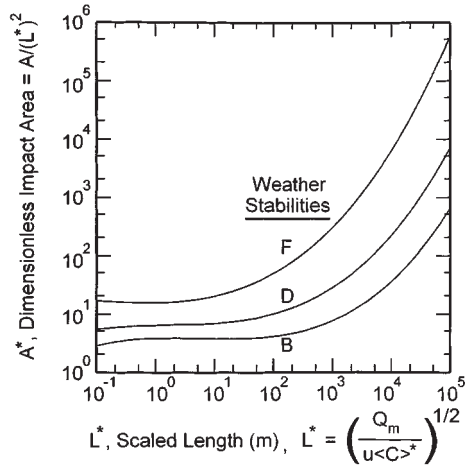


FIG. 26-59 Nomograph to determine the area affected by a release. (*Adapted from* Guidelines for Chemical Process Quantitative Risk Analysis, *1989, p. 91. Used by permission of the American Institute of Chemical Engineers.*)

1. Assume that all of the dispersion coefficients become equal at the virtual source. Then, from Eq. (26-63)

$$\sigma_y(y_v) = \sigma_z(z_v) = \left(\frac{Q_m}{\pi u \langle C\rangle^\circ}\right)^{1/2} \tag{26-69}$$

The virtual distances, y_v and z_v, determined using Eq. (26-69) are added to the actual downwind distance x to determine the dispersion coefficients σ_y and σ_z for subsequent computations.

2. Assume that $x_v = y_v = z_v$. Then, from Eq. (26-63)

$$\sigma_y(x_v) \cdot \sigma_z(x_v) = \frac{Q_m}{\pi u \langle C\rangle^\circ} \tag{26-70}$$

x_v is determined from Eq. (26-70) using a trial-and-error approach. The effective distance downwind for subsequent calculations using Eq. (26-63) is determined from $(x + x_v)$.

3. For large downwind distances, the virtual distances will be negligible and the point source models are used directly.

Strengths and Weaknesses The major strength to the gaussian approach is that the method is easy to apply. For most cases of interest, i.e., centerline concentrations along the ground, the equations reduce to a very simple form.

The primary weakness of the approach is that it does not apply to dense vapor releases, a category which includes most hydrocarbon materials. Furthermore, the concentrations predicted are time-weighted averages, with instantaneous values potentially exceeding the average. Finally, the range of applicability is typically from 0.1 to 10 km downwind from the release.

Example 1: Continuous Release What continuous release of chlorine is required to result in a concentration of 0.5 ppm at 300 m directly downwind on the ground? Also, estimate the total area affected. Assume that the release occurs at ground level and that the atmospheric conditions are worst case.

From Eq. (26-63), with $H_r = 0$, $z = 0$, and $y = 0$,

$$\langle C\rangle(x,0,0) = \frac{Q_m}{\pi \sigma_y \sigma_z u}$$

Worst-case atmospheric conditions occur to maximize $\langle C\rangle$. This occurs with minimum dispersion coefficients and minimum wind speed u within a stability class. By inspection of Figs. 26-54 and 26-55 and Table 26-28, this occurs with *F*-stability and $u = 2$ m/s. At 300 m = 0.3 km, from Figs. 26-54 and 26-55, σ_y = 11 m and $\sigma_z = 5$ m. The concentration in ppm is converted to kg/m^3 by application of the ideal gas law. A pressure of 1 atm and temperature of 298 K are assumed.

$$\text{mg/m}^3 = \left(\frac{\text{gm-mole K}}{0.08206\ \text{L atm}}\right)\left(\frac{PM}{T}\right)C_{\text{ppm}}$$

Using a molecular weight of 70.91 gm/gm-mole, the preceding equation gives a concentration of 1.45 mg/m^3. The release rate required is computed directly:

$$Q_m = \langle C\rangle^\circ \pi \sigma_y \sigma_z u = (1.45\ \text{mg/m}^3)(3.14)(11\ \text{m})(5\ \text{m})(2\ \text{m/s}) = 500\ \text{mg/s}$$

This is a very small release rate and demonstrates that it is much more effective to prevent the release than to mitigate it after the fact.

The area affected is determined from Fig. 26-59. For this case,

$$L^\circ = \left[\frac{5 \times 10^{-4}\ \text{kg/s}}{(2\ \text{m/s})(1.45 \times 10^{-6}\ \text{kg/m}^3)}\right]^{1/2} = 13.1\ \text{m}$$

From Fig. 26-59, $A^\circ = 20$ and it follows that

$$A = A^\circ (L^\circ)^2 = (20)(13.1\ \text{m})^2 = 3430\ \text{m}^2$$

Dense Gas Dispersion A dense gas is defined as any gas whose density is greater than the density of the ambient air through which it is being dispersed. This result can be due to a gas with a molecular weight greater than that of air, or a gas with a low temperature due to autorefrigeration during release, or other processes.

Dense gases behave considerably differently from neutrally buoyant gases. When they are initially released, these gases slump toward the ground and move both upwind and downwind. Furthermore, the mechanisms for mixing with air are completely different from neutrally buoyant releases.

As dense clouds move downwind, they are diluted with air until they eventually become neutrally buoyant. Thus, the gaussian models presented earlier are applicable for dense cloud releases at distances far downwind from the release.

A complete analysis of dense gas dispersion is much beyond the scope of this treatise. More detailed references are available (Britter and McQuaid, *Workbook on the Dispersion of Dense Gases,* Health and Safety Executive Report No. 17/1988, England, 1988; Lees, 1986, pp. 455–461; Hanna and Drivas, 1987; *Workbook of Test Cases for Vapor Cloud Source Dispersion Models,* AIChE, 1989; *Guidelines for Chemical Process Quantitative Risk Analysis,* 1989, pp. 96–103).

Many computer codes, both public and private, are available to model dense cloud dispersion. A detailed review of these codes, and how they perform relative to actual field test data, is available (Hanna, Chang, and Strimaitis, *Atmospheric Environment,* vol. 27A, no. 15, 1993, pp. 2265–2285). An interesting result of this review is that a simple nomograph method developed by Britter and McQuaid (1988) matches the available data as well as any of the computer codes. This method will be presented here.

The Britter and McQuaid model was developed by performing a dimensional analysis and correlating existing data on dense cloud dispersion. The model is best suited for instantaneous or continuous ground-level area or volume source releases of dense gases. Atmospheric stability was found to have little effect on the results and is not a part of the model. Most of the data came from dispersion tests in remote, rural areas, on mostly flat terrain. Thus, the results would not be applicable to urban areas or highly mountainous areas.

The model requires a specification of the initial cloud volume, the initial plume volume flux, the duration of release, and the initial gas density. Also required is the wind speed at a height of 10 m, the distance downwind, and the ambient gas density.

The first step is to determine if the dense gas model is applicable. If an initial buoyancy is defined as

$$g_o = \frac{g(\rho_o - \rho_a)}{\rho_a} \tag{26-71}$$

and a characteristic source dimension as, for continuous releases,

$$D_c = \left(\frac{q_o}{u}\right)^{1/2} \tag{26-72}$$

and for instantaneous releases:

$$D_i = V_o^{1/3} \tag{26-73}$$

then the criteria for a sufficiently dense cloud to require a dense cloud representation are, for continuous releases:

$$\left(\frac{g_o q_o}{u^3 D_c}\right)^{1/3} \geq 0.15 \tag{26-74}$$

and for instantaneous releases:

$$\frac{(g_o V_o)^{1/2}}{u D_i} \geq 0.20 \tag{26-75}$$

If these criteria are satisfied, then Figs. 26-60 and 26-61 are used to estimate the downwind concentrations.

The criteria for determining whether the release is continuous or instantaneous is calculated using the following group:

$$\frac{uR_d}{x} \tag{26-76}$$

If the group has a value greater than or equal to 2.5, then the dense gas release is considered continuous. If the group value is less than or equal to 0.6, then the release is considered instantaneous. If the value lies in between, then the concentrations are calculated using both continuous and instantaneous models and the minimum concentration result is selected.

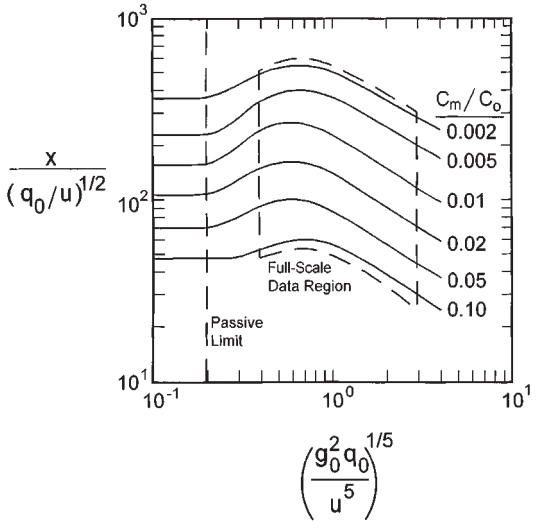


FIG. 26-60 Nomograph to estimate downwind concentrations due to continuous dense gas release based on the Britter-McQuaid correlation.

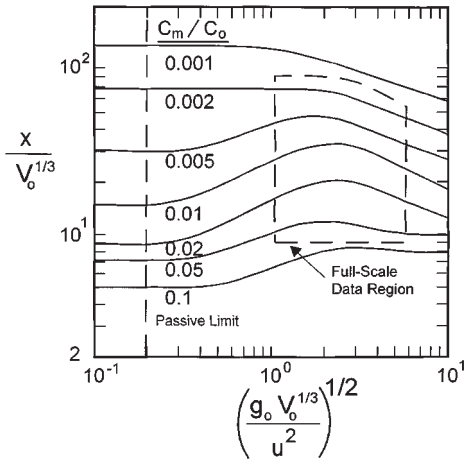


FIG. 26-61 Nomograph to estimate downwind concentrations due to an instantaneous dense gas release based on the Britter-McQuaid correlation.

The Britter and McQuaid model is not appropriate for jets or two-phase plume releases. However, it would be appropriate at a minimal distance of 100 m from these types of releases since the initial release effect is usually minimal beyond these distances.

Example 2: LNG Dispersion Tests Britter and McQuaid (1988, p. 70) report on the Burro LNG dispersion tests. Compute the distance downwind from the following LNG release to obtain a concentration equal to the lower flammability limit (LFL) of 5 percent vapor concentration by volume. Assume ambient conditions of 298 K and 1 atm. The following data are available:

Spill rate of liquid	0.23 m^3/s
Spill duration R_d	174 s
Windspeed at 10 m above ground (u)	10.9 m/s
LNG density	425.6 kg/m^3
LNG vapor density at boiling point of −162°C	1.76 kg/m^3

Solution. The volumetric discharge rate is given by:

$$q_o = \frac{(0.23\ m^3/s)(425.6\ kg/m^3)}{1.76\ kg/m^3} = 55.6\ m^3/s$$

The ambient air density is computed from the ideal gas law and gives a result of 1.22 kg/m^3. Thus

$$g_o = g\left(\frac{\rho_o - \rho_a}{\rho_a}\right) = (9.8\ m/s^2)\left(\frac{1.76 - 1.22}{1.22}\right) = 4.29\ m/s^2$$

Step 1: Determine if the release is considered continuous or instantaneous. For this case, Eq. (26-76) applies and the quantity must be greater than 2.5 for a continuous release. Thus

$$\frac{uR_d}{x} = \frac{(10.9\ m/s)(174\ s)}{x} \geq 2.5$$

and it follows that for a continuous release

$$x \leq 758\ m$$

Our final distance must be less than this for application of the continuous release model.

Step 2: Determine if a dense cloud model applies. For this case, Eqs. (26-69) and (26-74) apply. Substituting the appropriate numbers,

$$D_c = \left(\frac{q_o}{u}\right)^{1/2} = \left(\frac{55.6\ m^3/s}{10.9\ m/s}\right)^{1/2} = 2.26\ m$$

$$\left(\frac{g_o q_o}{u^3 D_c}\right)^{1/3} = \left[\frac{(4.29\ m/s^2)(55.6\ m^3/s)}{(10.9\ m/s)^3(2.26\ m)}\right]^{1/3} = 0.43 \geq 0.15$$

and it is clear that the dense cloud model applies.

Step 3: Adjust the concentration for non-isothermal release. Britter and MacQuaid (1988, p. 61) provide an adjustment to the concentration to account

for non-isothermal release of the vapor. If the original, non-isothermal concentration is C^*, then the equivalent isothermal concentration is given by

$$C = \frac{C^*}{C^* + (1 - C^*)(T_a/T_o)}$$

where T_a is the ambient temperature and T_o is the source temperature. For our required concentration of 0.05, the preceding equation gives an effective concentration of 0.019.

Step 4: Compute the dimensionless groups for Fig. 26-61.

$$\left(\frac{g_o^2 q_o}{u^5}\right)^{1/5} = \left[\frac{(4.29\ \text{m/s}^2)^2(55.6\ \text{m}^3/\text{s})}{(10.9\ \text{m/s})^5}\right]^{1/5} = 0.367$$

and

$$\left(\frac{q_o}{u}\right)^{1/2} = \left(\frac{55.6\ \text{m}^3/\text{s}}{10.9\ \text{m/s}}\right)^{1/2} = 2.25\ \text{m}$$

Step 5: Apply Fig. 26-60 to determine the downwind distance. The initial concentration of gas C_o is essentially pure LNG. Thus, $C_o = 1.0$ and it follows that $C_m/C_o = 0.019$. From Fig. 26-60,

$$\frac{x}{\left(\frac{q_o}{u}\right)^{1/2}} = 126$$

and it follows that $x = (2.25\ \text{m})(126) = 283$ m. This compares to an experimentally determined distance of 200 m. This demonstrates that dense gas dispersion estimates can easily be off by a factor of 2. A gaussian plume model assuming worst-case weather conditions (*F*-stability, 2 m/s wind speed) predicts a downwind distance of 14 km. Clearly, the dense cloud model provides a much better result.

DISCHARGE RATES FROM PUNCTURED LINES AND VESSELS

Nomenclature

a, b, c	Constants
A	Cross-sectional area perpendicular to flow, m^2
C_D	Overall discharge coefficient (–)
C_{DG}	Discharge coefficient for gas flow (–)
C_{DL}	Discharge coefficient for liquid flow (–)
C_p	Heat capacity at constant pressure, $J\cdot kg^{-1}\cdot K^{-1}$
C_v	Heat capacity at constant volume, $J\cdot kg^{-1}\cdot K^{-1}$
D	pipe diameter, m
D_T	tank diameter, m
f	Fanning friction factor (–)
F_I	Pipe inclination factor, Eq. (26-87)
g	Gravitational acceleration, ms^{-2}
G	Mass flux, $kg\cdot m^{-2}$, s^{-1}
H	Specific enthalpy, $J\cdot kg^{-1}$
H_{GL}	Heat of vaporization, $(H_G - H_L)$ sat, $J\cdot kg^{-1}$
k	Value near C_p/C_v
K	Slip velocity ratio, u_G/u_L
K_e	Number of velocity heads for fittings, expansions, contractions, and bends
L	Length of pipe
N	$4fL/D + K_e$
P	Pressure, $N\cdot m^{-2}$
q	Constant
Q	Heat transfer rate, W/kg
R	Gas constant, $Jk\ mole^{-1}K^{-1}$
Re	Reynolds number, $G\cdot D/\mu$ (–)
S	Entropy, $J\cdot kg^{-1}\cdot K^{-1}$
t	Time, s
T	Temperature, K
u	Velocity, ms^{-1}
v	Specific volume, $m^3\cdot kg^{-1}$
w	Mass discharge rate, $kg\cdot s^{-1}$
x	Vapor quality, kg vapor/kg mixture
X_m	Lockhart Martinelli parameter
z	Vertical distance, m

Greek	
α	Vapor void fraction, m^3 vapor/m^3 mixture
γ	Heat capacity ratio, C_p/C_v
ε	Dimensionless specific volume, v/v_o
η	Pressure ratio, P/P_o
θ	Inclination angle of pipe to horizontal
μ	Two-phase viscosity, P
ρ	Density, $kg\cdot m^{-3}$
σ	Area ratio
ϕ	Two-phase multiplier, pressure drop for two-phase flow divided by pressure drop for single-phase flow
ω	Parameter defined by Eqs. (26-90) or (26-91)

Subscripts	
a	Ambient
c	Choked
d	Discharge
g, G	Gas or vapor
GL	Gas minus liquid
H	Homogeneous
L	Liquid
N	Nonequilibrium or puncture area
o	Area initial, stagnation conditions
p	Pipe flow
s	Saturation
1	Point at which backpressure from pipe is felt after entrance from tank
2	Plane at vena contracta or at pipe puncture
*	Dimensionless

General References: Cheremisinoff and Gupta, eds., *Handbook of Fluids in Motion,* Ann Arbor Science, Ann Arbor, Michigan, 1983. Chisholm, *Two-phase Flow in Pipelines and Heat Exchangers,* George Godwin, New York, in association with the Institution of Chemical Engineers, 1983. Fisher et al., *Emergency Relief System Design Using DIERS Technology,* AIChE, New York, 1992. Graham, "The Flow of Air-Water Mixtures Through Nozzles," National Engineering Laboratories (NEL) Report No. 308, East Kilbride, Glasgow, 1967. Jobson, "On the Flow of Compressible Fluids Through Orifices," *Proc. Instn. Mech. Engrs.* **169**(37): 767–776, 1955. "The Two-Phase Critical Flow of One-Component Mixtures in Nozzles, Orifices, and Short Tubes," *Trans. ASME, J. Heat Transfer* **93**(5): 179–N87, 1976. Lee and Sommerfeld, "Maximum Leakage Times Through Puncture Holes for Process Vessels of Various Shapes," *J. Hazardous Materials* **38**(1): 27–40, July 1994. Lee and Sommerfeld, "Safe Drainage or Leakage Considerations and Geometry in the Design of Process Vessels," *Trans. IChemE* **72,** part B: 88–89, May 1994. Leung, "A Generalized Correlation for One-Component Homogeneous Equilibrium Flashing Choked Flow," *AIChE J.* **32**(10): 1743–1746, 1986. Leung, "Similarity Between Flashing and Non-flashing Two-Phase Flow," *AIChE J.* **36**(5): 797, 1990. Leung, "Size Safety Relief Valves for Flashing Liquids," *Chem. Eng. Prog.* **88**(2): 70–75, February 1992. Leung, "Two-Phase Flow Discharge in Nozzles and Pipes—A Unified Approach," *J. Loss Prevention Process Ind.* **3**(27): 27–32, January 1990. Leung and Ciolek, "Flashing Flow Discharge of Initially Subcooled Liquid in Pipes," *ASME Trans. J. Fluids Eng.* **116**(3), September 1994. Leung and Epstein, "Flashing Two-Phase Flow Including the Effects of Noncondensable Gases," *ASME Trans. J Heat Transfer* **113**(1): 269, February 1991. Leung and Epstein, "A Generalized Correlation for Two-Phase Non-flashing Homogeneous Choked Flow," *ASME J. Heat Transfer* **112**(2), May 1990. Leung and Grolmes, "The Discharge of Two-Phase Flashing Flow in a Horizontal Duct," *AIChE J.* **33**(3): 524–527, 1987; also errata, **34**(6): 1030, 1988. Leung and Grolmes, "A Generalized Correlation for Flashing Choked Flow of Initially Subcooled Liquid," *AIChE J.* **34**(4): 688–691, 1988. Levenspiel, "The Discharge of Gases from a Reservoir Through a Pipe," *AIChE J.* **23**(3): 402–403, 1977. Lockhart and Martinelli, "Proposed Correlation of Data for Isothermal Two-Phase, Two-Component Flow in Pipes," *Chem. Eng. Prog.* **45**(1): 39–48, January 1949. Sozzi and Sutherland, "Critical Flow of Saturated and Subcooled Water at High Pressure, General Electric Co. Report No. NEDO-13418, July 1975; also *ASME Symp. on Non-equilibrium Two-Phase Flows,* 1975. Tangren, Dodge, and Siefert, "Compressibility Effects in Two-Phase Flow," *J. Applied Physics* **20:** 637–645, 1949. Uchida and Narai, "Discharge of Saturated Water Through Pipes and Orifices," *Proc. 3d Intl. Heat Transfer Conf.,* ASME, Chicago, **5:** 1–12, 1966. Van den Akker, Snoey, and Spoelstra, "Discharges of Pressurized Liquefied Gases Through Apertures and Pipes," *I. Chem. E. Symposium Ser.* (London), **80:** E23–35, 1983. Watson, Vaughan, and McFarlane, "Two-Phase Pressure Drop with a Sharp-Edged Orifice," National Engineering Laboratories (NEL) Report No. 290, East Kilbride, Glasgow, 1967. Woodward, "Discharge Rates Through Holes in Process Vessels and Piping," in V. Fthenakis, ed., *Prevention and Control of Accidental Releases of Hazardous Gases,* Van Nostrand Reinhold, New York, pp. 94–159, 1993. Woodward and Mudan, "Liquid and Gas Discharge Rates Through Holes in Process Vessels," *J. Loss Prevention:* **4**(3): 161–165, 1991.

Overview Modeling the consequences of accidental releases of hazardous materials begins with the calculation of discharge rates. In the most general case, the discharged material is made up of a volatile flashing liquid and vapor along with noncondensable gases and solid particles. For efficiency, the treatment here is of two-phase flow, which reduces as a special case to single-phase all gas or all liquid flow. Solid particulate discharge is usually not particularly hazardous and is not considered here.

If the puncture occurs on a pipe which is at least 0.5 m from a vessel, it is justifiable to use a *homogeneous equilibrium model* (HEM) for which an analytical solution is available. The discharge rate pre-

dictions by the HEM beyond this range are within 10 percent of measured values for single-component liquids which are either subcooled or saturated.

If the puncture occurs on the vessel or on a line shorter than 0.5 m, the discharge is likely to be nonhomogeneous, meaning the gas and liquid velocities are not equal and the phases are not likely to be in equilibrium. For this case, various models have been developed, including some of considerable complexity, accounting for interphase heat, mass, and momentum transfer. These are generally used in the nuclear power industry. For most engineering applications, simpler models suffice. A reasonably simple *nonequilibrium model* (NEM) is developed here. We also provide an HEM for orifice flow, since it helps to develop the HEM for pipe flow, and its inaccuracies may at times be tolerable.

The energy and momentum balances common to both situations are stated first, along with some useful general concepts, followed by a development of an HEM for orifice and pipe discharge by Leung (1986; 1990; 1992) and Leung et al. (Leung and Ciolek, 1994; Leung and Epstein, 1990; Leung and Grolmes, 1988) and then the NEM for short pipe, orifice, and nozzle flow summarized by Chisholm.

Discharge Flow Regimes Upon developing a puncture in either the vessel or a line attached to the vessel, as in Fig. 26-62, the subsequent depressurization can cause a volatile liquid to flash and develop bubbles in the liquid. These bubbles cause an expansion, or *swell,* which raises the two-phase, or *frothy,* level. If the puncture is in the vapor space of a vessel or on a line from the vapor space, the discharge will be at least initially all vapor. This is the simplest discharge case and is treated here as a special case.

In the more general and more difficult case, either the puncture is initially in the liquid space, or in a line attached to it, or the liquid swells to reach the puncture or punctured line, giving two-phase or all-liquid discharge. For these cases the discharge model solutions must treat four regimes, which are defined by the initial void (vapor) fraction α_o and by the pressure ratios:

$$\eta_s = \frac{P_s}{P_o} \qquad \eta_a = \frac{P_a}{P_o}$$

where P_s is the saturation vapor pressure and P_a is ambient pressure.

Regime 1. If the tank is initially saturated (usually pressurized with volatile contents) there is no padding gas contributing noncondensables, so $\eta_s = 1$ and $\alpha_o = 0$. In this case, a discharge in the liquid space is a flashing liquid.

If the initial tank conditions are subcooled, $\eta_s < 1$, tank pressure must be maintained with padding gas (which could be air), typically introducing noncondensables, so $\alpha_o > 0$. These noncondensables may or may not become involved in the discharge. Furthermore, the subcooled liquid may flash ($\eta_s > \eta_a$) or not ($\eta_s < \eta_a$). In addition, some reacting systems generate noncondensable gases, giving Regimes 3 or 4.

Regime 2. If the puncture is below the initial liquid level, the padding gas will not be discharged, so there will be no noncondensables in the discharge ($\alpha_o = 0$). With low or moderate subcooling, $\eta_s > \eta_a$, the subcooled liquid will flash when the pressure ratio at some point drops below η_s. This point could be beyond the choke point, though. With high subcooling, $\eta_s < \eta_a$, and no flashing occurs (single-phase flow).

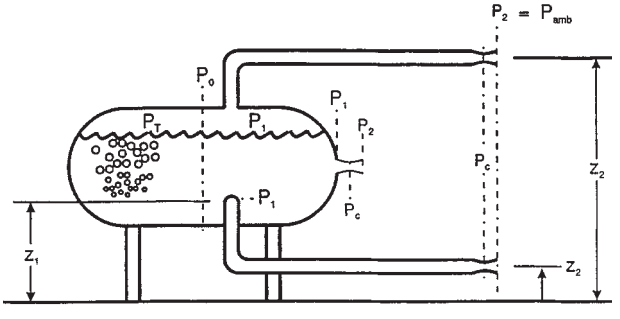


FIG. 26-62 Definition of terms for puncture of a vessel or line attached to a vessel.

Regime 3. If the puncture is above the initial liquid level but becomes covered by the swell, there will be noncondensables mixed with the liquid ($\alpha_o > 0$). If also $\eta_s < \eta_a$, no flashing occurs. This is called a *frozen flow situation,* since the mass fraction of compressible component x_o is constant during discharge.

Regime 4. This is the same as Regime 3 ($\alpha_o > 0$) except $1 < \eta_s < \eta_a$, so flashing occurs, giving two sources of compressible gases and vapors.

Solutions are given here for only the first three regimes. For Regime 4, see Leung and Epstein (1991).

Figures 26-63 and 26-64 illustrate the significant differences between subcooled and saturated-liquid discharge rates. Discharge rate decreases with increasing pipe length in both cases, but the drop in discharge rate is much more pronounced with saturated liquids. This is because the flashed vapor effectively chokes the flow and decreases the two-phase density.

General Two-Phase Flow Relationships For flow across an orifice or nozzle, the equilibrium mass fraction of flashed vapor x can be found for single components from either an entropy or an enthalpy balance. For multicomponents, use a standard flash routine. Since orifice discharge follows a more nearly isentropic thermodynamic path, the appropriate balance to use for single components in this case is the entropy balance (Van den Akker, Snoey, and Spoelstra, 1983). This balance is written from the initial stagnation point inside the vessel with temperature T_o to the saturation temperature T_s at a given pressure (of greatest interest are the choke pressure or ambient pressure). This gives:

$$x = \frac{S_{Lo}(T_o) - S_L(T_s)}{S_{GL}(T_s)} \tag{26-77}$$

At ambient pressure, T_s is the normal boiling point.

Since pipe flow is more nearly isenthalpic, the flash fraction x is found from an enthalpy balance between the stagnation point and a point z downstream. Accounting for changes in potential energy, kinetic energy, and heat added or removed from the pipe Q, x is given by:

$$x = \frac{H_{Lo}(T_o) - H_{L2}(T_{S2}) - \tfrac{1}{2}u_{L2}^2 - gz\sin\theta + Q}{H_{GL}(T_{s2}) + \tfrac{1}{2}u_{G2}^2 - \tfrac{1}{2}u_{L2}^2} \tag{26-78}$$

If the potential energy, kinetic energy, and heat added terms are negligible, this reduces to:

$$x = \frac{H_{Lo}(T_o) - H_L(T_s)}{H_{GL}(T_s)} \tag{26-79}$$

These equations apply also to multicomponent systems, where the enthalpies are found for each phase from the component enthalpies.

Figure 26-62 depicts a flow system, which is described by the following differential momentum balance:

$$vdP + G^2 v dv + \left[4f_{Lo}\frac{dz}{D} + K_e\right]\frac{1}{2}G^2 v_{Lo}^2 \phi_{Lo}^2 + g\sin\theta dz = 0 \tag{26-80}$$

where the terms represent the effect of pressure gradient, acceleration, line friction, and potential energy (static head), respectively. The effect of fittings, bends, entrance effects, etc., is included in the term K_e by standard methods. The inclination angle θ is the angle to the horizontal of a line from the pipe connection at the vessel to the discharge point. The term ϕ_{Lo}^2 is the two-phase multiplier which corrects the liquid-phase friction pressure loss to a two-phase pressure loss. Converting Eq. (26-80) to the dimensionless variables:

$$G_*^2 = \frac{G^2}{P_o\rho_o}, \qquad \eta = \frac{P}{P_o}, \qquad \varepsilon = \frac{v}{v_o} \tag{26-81}$$

gives:
$$\varepsilon d\eta + G_*^2 \varepsilon d\varepsilon + N\frac{1}{2}G_*^2\varepsilon^2\phi_{Lo}^2 + \frac{g\sin\theta dz}{P_o v_o} = 0 \tag{26-82}$$

where N is the number of equivalent velocity heads, given by:

$$N = 4f_{Lo}\frac{dz}{D} + K_e \tag{26-83}$$

For homogeneous flow, the two-phase multiplier is simply:

$$\phi_{FLO}^2 = \frac{v_H}{v_L} \tag{26-84}$$

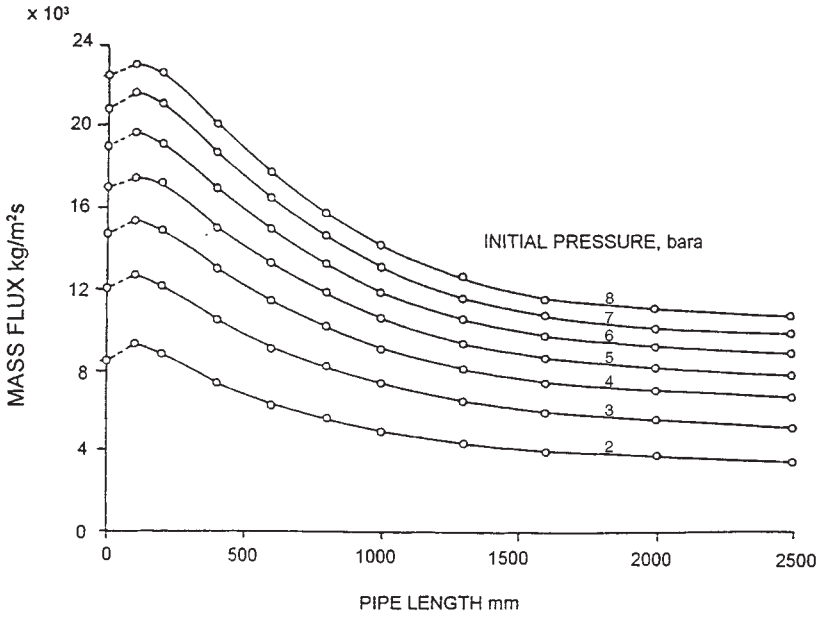


FIG. 26-63 Discharge mass flux for highly subcooled water (20°C) from orifice and 4-mm pipe of various lengths. (*Data of Uchida and Narai, 1966; reproduced by permission of ASME.*)

where v_H is the homogeneous specific volume given by:

$$v_H = xv_G + (1 - x)\, v_L \tag{26-85}$$

The momentum balance for homogeneous flow can be factored to a form which enables integration as:

$$-N = \frac{G_{\circ\rho}^2 \varepsilon_H d\varepsilon_H + \varepsilon_H d\eta}{\tfrac{1}{2} G_{\circ\rho}^2 \varepsilon_H^2 + F_I} \tag{26-86}$$

by defining a pipe inclination factor F_I:

$$F_I = \frac{gD \sin \theta}{4 f_{Lo} P_o v_o} \tag{26-87}$$

F_I is positive for upflow, negative for downflow, and zero for horizontal flow.

The energy balance across a pipe from the stagnation point 0 to a point 2 downstream is:

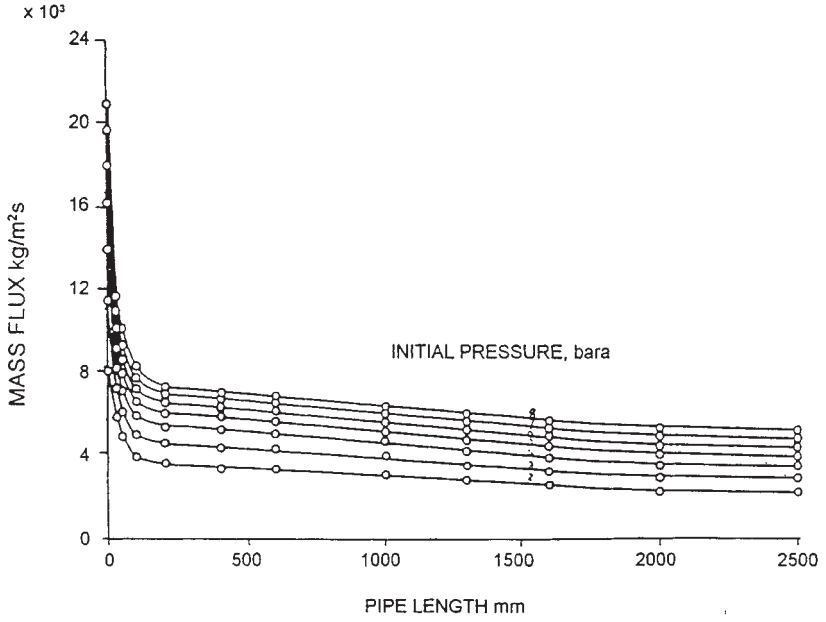


FIG. 26-64 Discharge mass flux for saturated water from orifice and 4-mm pipe of various lengths. (*Data of Uchida and Narai, 1966; reproduced by permission of ASME.*)

$$H_o + \frac{1}{2} u_o^2 = \frac{1}{2} (G^2 v_e^2)_2 + H_2 + Q \tag{26-88}$$

For homogeneous flow, the equivalent specific volume v_e is the same as the homogeneous specific volume v_H, and the enthalpy is given by:

$$H_2 = [xH_G + (1 - x) H_L]_2 \tag{26-89}$$

Omega Method HEM Equation (26-86) can be integrated after first relating the dimensionless specific volume ε to the dimensionless pressure ratio η. A simple reciprocal relationship, designated the *omega method*, was suggested by Leung (1986) and by Leung and Grolmes (1988):

$$\varepsilon_H = \begin{cases} \omega \left[\dfrac{\eta_s}{\eta} - 1 \right] + 1 & \text{if } \dfrac{\eta_s}{\eta} > 1 \\ 1.0 & \text{if } \dfrac{\eta_s}{\eta} \le 1 \end{cases} \tag{26-90}$$

Figure 26-65 illustrates that Eq. (26-90) provides a linear approximation to the nonlinear relationship between two-phase specific volume and reciprocal pressure (v_H vs. P^{-1} or ε_H vs. η^{-1}). For single components, the initial slope of the ε_H curve is found using the Clapeyron equation to give:

$$\omega = \alpha_o + (1 - \alpha_o)\, \omega_s$$

$$\alpha_o = x_o \frac{v_{vo}}{v_o}$$

$$\omega_s = \frac{C_{PL}\, T_o P_s}{v_{LO}} \left[\frac{v_{VLO}\,(P_s)}{h_{VLO}\,(P_s)} \right]^2 \tag{26-91}$$

To generalize for multicomponents and, in fact, to find a better fit for single components, use known information about the value of ε_H at some lower pressure, $\eta = \eta_2$, where η_2 is a rough approximation to the choking pressure ratio. That is, use the slope over the largest pressure interval of interest to give:

$$\omega = \frac{\varepsilon_2 - 1}{(\eta_s/\eta_2) - 1} \tag{26-92}$$

Equation (26-91) gives values which are often high or low at the low-pressure end of the curve, whereas Eq. (26-92) is in error only insofar as the true ε curve is nonlinear. However, in practice, either approach provides adequate predictions for discharge rate.

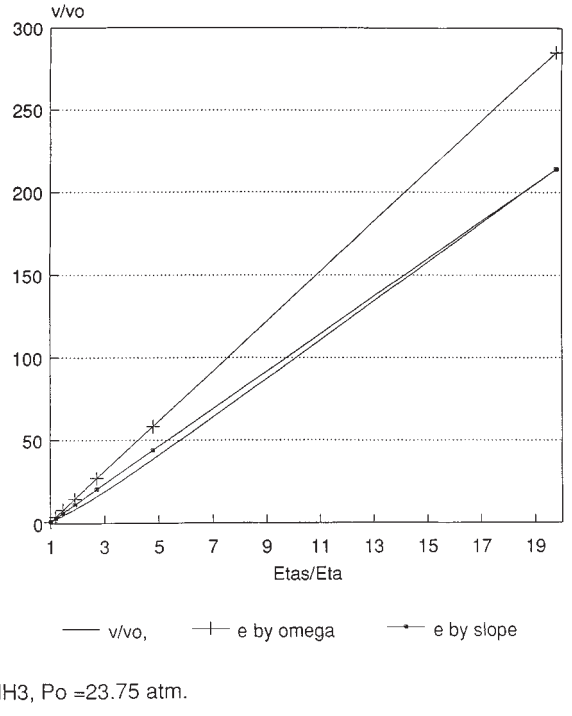


FIG. 26-65 Comparison of predictions for two-phase specific volume as a function of pressure by the omega method for two alternative formulas to calculate omega.

HEM for Two-Phase Orifice Discharge For orifice or nozzle flow, the friction term and the potential energy term in Eq. (26-82) are negligible, so it can be integrated in general across both subcooled and flashing regions thusly:

$$\frac{1}{2} \frac{G_{\circ ori}^2}{C_D^2} \varepsilon_2^2 = \int_1^{\eta_s} \varepsilon_H\, d\eta + \int_{\eta_s}^{\eta_2} \varepsilon_H\, d\eta \tag{26-93}$$

For the highly subcooled subset of Regime 2, ($\eta_s < \eta_a$), flow is single-phase (liquid), and integration of Eq. (26-93) gives what is commonly referred to as the *orifice equation:*

Subcooled Liquid Orifice Discharge

$$G_{\circ ori}^2 = C_D^2 2\,(1 - \eta_2) \tag{26-94}$$

For the compressible flow cases, Regimes 1 and 3, and Regime 2 with $\eta_s > \eta_a$, making use of Eq. (26-90), integration of Eq. (26-93) gives:

Compressible Fluid Orifice Discharge by HEM

$$\frac{G_{\circ ori}^2}{C_D^2} = \frac{2\,\{(1 - \eta_{sp}) + (1 - \omega)\,(\eta_{sp} - \eta_2) + \omega\eta_{sp} \ln\,(\eta_{sp}/\eta_2)\}}{\varepsilon_2^2} \tag{26-95}$$

This is written with the general notation η_{sp} to avoid repetition of similar equations. For Regime 1, $\alpha_o = 0$, so $\omega = \omega_s$, and $\eta_{sp} = \eta_s$. For Regime 3, $\omega = \alpha_o$, and the integration is developed with $\eta_{sp} = 1$, so the above solution applies with $\eta_{sp} = 1$. This emphasizes the essential unity of the solution for Regimes 1 and 3. Equation (26-95) is plotted in Fig. 26-66 with Regime 1 to the right of $\omega = 1$ and Regime 3 to the left.

Equation (26-95) applies for subsonic as well as choked flow. Choked flow occurs at the pressure ratio $\eta_2 = \eta_c$, which maximizes $G_{\circ ori}$. To maximize $G_{\circ ori}$, differentiate Eq. (26-95) and set:

$$\left[\frac{\partial G_\circ}{\partial \eta_2} \right]_{\eta_2 = \eta_c} = 0 \tag{26-96}$$

This gives a transcendental equation in η, the root of which occurs when $\eta = \eta_c$:

$$\frac{(1 - \omega)^2}{2\omega\eta_s} \eta^2 + 2\,(1 - \omega)\,\eta + \left(\frac{3}{2}\omega\eta_s - 1 \right) - \omega\eta_s \ln \frac{\eta_s}{\eta} = 0 \tag{26-97}$$

Use a root-finding algorithm to discover the value of η_c which satisfies Eq. (26-97). These values are also plotted in Fig. 26-66.

For Regime 2, $\alpha_o = 0$ and $\omega = \omega_s$. Regime 2 requires using the incompressible solution for highly subcooled liquids and the compressible flow solutions for liquids of a low degree of subcooling. Essentially, these provide two branches to the solution, and by the flow maximization principle, we must choose the larger of the two. Empirically, the point at which these branches of the solution cross is given by:

$$\eta_{st} = \frac{2\omega\eta_s}{1 + 2\omega\eta_s} \tag{26-98}$$

So, when $\eta_s > \eta_{st}$ (low subcooling, flashing before the choke print), use the compressible solution, Eq. (26-95) with $\eta_{sp} = \eta_s$. Otherwise (for high subcooling, no flashing before the choke point), use the liquid orifice equation, Eq. (26-94).

The solution for Regime 2 is plotted in Fig. 26-67. The high subcooling branch given by the liquid orifice equation goes through $G_{\circ ori} = 0$ when $\eta_s = 1$. The moderate subcooling branch parts with the former branch at η_{st} and matches values shown in Figure 26-66 when $\eta_s = 1$.

Choked Flow by Two-Phase Energy Balance From the energy balance, Eq. (26-88), taking $u_o = 0$ (stagnation) and $Q = 0$:

$$G_{ori} = \frac{[2\,(H_o - H_2)]^{1/2}}{v_e} \tag{26-99}$$

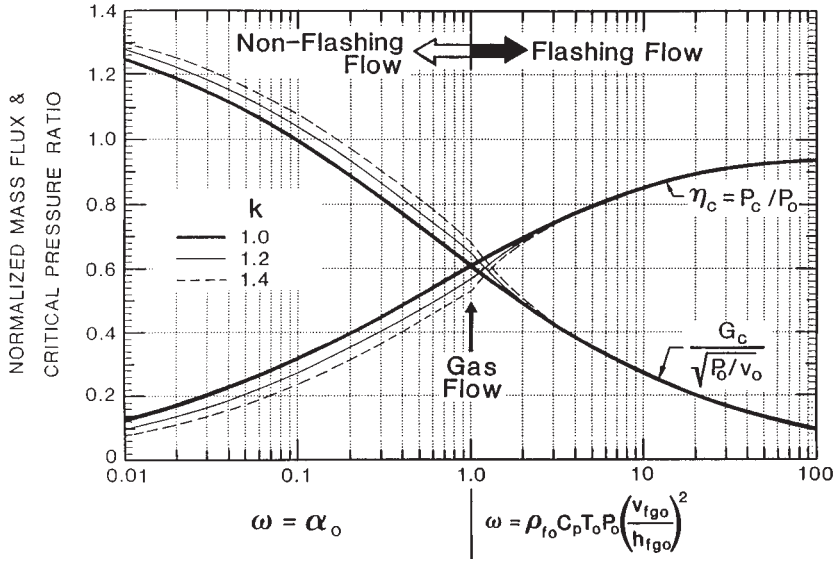


FIG. 26-66 Normalized mass flux and choked flow pressure ratio for frozen flow (left side) and for flashing liquid flow (right side) from orifice or nozzle discharge by the homogeneous equilibrium model. (*Leung, J.C.,* Chem. Eng. Progress ***88****(2), pp. 70–75, 1992, Reproduced with permission of AIChE. Copyright 1992 AIChE. All rights reserved.*)

where v_e is an equivalent specific volume. This provides a simple alternative HEM for finding mass flux. Simply decrement pressure and search for the maximum value of G given by Eq. (26-99). This method requires good physical properties tables.

Differentiating with respect to pressure and invoking the first law of thermodynamics gives:

$$G_{\text{ori}}^2 = \frac{-1}{v_e}\left(\frac{\partial H}{\partial v_e}\right)_s = -\left[\frac{\partial P}{\partial v_e}\right]_s \tag{26-100}$$

or equivalently, differentiating Eq. (26-90) with respect to (η_2) gives:

$$G_{\text{ori}}^2 = -\left[\frac{\partial \varepsilon}{\partial \eta}\right]_s^{-1} = \frac{\eta_2^2}{\omega \eta_s} \tag{26-101}$$

When the flow is choked, this equation gives the same value for G_{ori} as does Eq. (26-95), as long as the root of Eq. (26-97) η_c is substituted for η_2.

Full-Bore and Punctured Pipe Discharge With a pipe puncture, the mass flux at the discharge point G_{ed} is larger than the mass flux in the pipe G_{ep}, by the puncture–to–pipe area ratio A_N/A_p, or $(D/D_p)^2$, defined as σ. Specifically:

$$G_{ep} = \sigma\, G_{ed} \tag{26-102}$$

Since this correction is readily made, the following discussion assumes a full-bore pipe rupture, or $\sigma = 1$.

HEM for Two-Phase Pipe Discharge With a pipe present, the backpressure experienced by the orifice is no longer η_2, but rather an intermediate pressure ratio η_1. Thus η_1 replaces η_2 in the orifice solution for mass flux G_{ori} Eq. (26-95). Correspondingly, the momentum balance is integrated between η_1 and η_2 to give the pipe flow solution for G_{ep}. The solutions for orifice and pipe flow must be solved simultaneously to make $G_{\text{ori}} = G_{ep}$ and to find η_1 and η_2. This can be done explicitly for the simple case of incompressible single-phase (liquid) inclined or horizontal pipe flow. The solution is implicit for compressible regimes.

For incompressible orifice flow, $\varepsilon_H = 1$ and Eq. (26-86) is integrated between 1 and η_1 to give Eq. (26-94), with η_1 replacing η_2. Equation (26-86) integrated between η_1 and η_2 gives:

$$G_{ep}^2 = \frac{2\,(\eta_1 - \eta_2)}{N} - 2F_i \tag{26-103}$$

Eliminating η_1 using Eq. (26-94) and setting $G_{\text{ori}} = G_{ep}$ and $C_D = 1$ gives:

Subcooled Liquid Inclined Pipe Discharge

$$G_{ep}^2 = \frac{2\,(1-\eta_2) - NF_I}{N+1} \tag{26-104}$$

For horizontal pipe flow, $F_I = 0$.

The general-case solution for compressible, inclined pipe flow is next stated, then the solution is developed for the special case of horizontal compressible flow.

Using the omega equation, Eq. (26-90), to eliminate $d\varepsilon_H$ in Eq. (26-86) enables Eq. (26-86) to be integrated to the following:

HEM for Inclined Pipe Discharge For = $\eta_1 > \eta_s > \eta_2$ (flashing within the pipe):

$$N + \ln\left[\frac{X(\eta_2)}{X(\eta_{sp})}\left[\frac{\eta_{sp}}{\eta_2}\right]^2\right] = \frac{(\eta_1 - \eta_{sp}) + (1-\omega)(\eta_{sp} - \eta_2)}{c} + \left[\frac{c\omega\eta_s - b(1-\omega)}{2c^2}\right]\ln\left[\frac{X(\eta_{sp})}{X(\eta_2)}\right]$$

$$= \left[\frac{(1-\omega)(b^2 - 2ac) - bc\omega\eta_s}{2c^2}\right][I_o(\eta_{sp}) - I_o(\eta_2)] \tag{26-105}$$

where:

$$X(\eta) = a + b\eta + c\eta^2 \tag{26-106}$$

$$a = \frac{1}{2} G_{ep}^2\, \omega^2 \eta_s^2 \tag{26-107}$$

$$b = \frac{1}{2} G_{ep}^2\, \omega\,(1-\omega)\,\eta_s \tag{26-108}$$

$$c = \frac{1}{2} G_{ep}^2\,(1-\omega)^2 + F_I \tag{26-109}$$

$$q = 4ac - b^2 \tag{26-110}$$

Defining:

$$I_o(\eta) = \int \frac{d\eta}{X(\eta)} \tag{26-111}$$

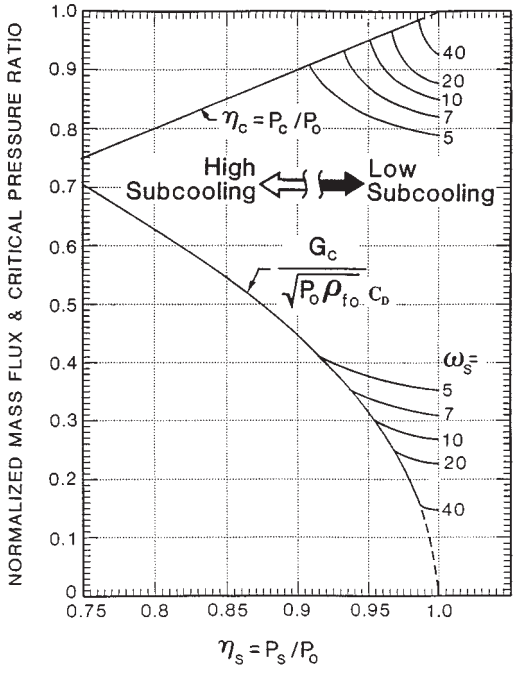


FIG. 26-67 Normalized mass flux and choked flow pressure ratio for flashing liquid discharge from orifices or nozzles by the homogeneous equilibrium model.(*Leung, J.C. and M.A. Grolmes,* AIChE J. **33***(3) pp. 524–527 (1987); Leung, J.C.,* Chem. Eng. Prog. **92***(12), pp. 28–50 (1996). Reproduced with permission of AIChE, Copyright 1987, 1996. All rights reserved.)*

we obtain:

$$I_o(\eta) = \begin{cases} \dfrac{2}{q^{1/2}} \tan^{-1}\left[\dfrac{2c\eta + b}{q^{1/2}}\right] & \text{if } q > 0 \text{ (upflow)} \\ \dfrac{1}{(-q)^{1/2}} \ln\left[\dfrac{2c\eta + b - (-q)^{1/2}}{2c\eta + b + (-q)^{1/2}}\right] & \text{if } q < 0 \text{ (downflow)} \end{cases} \quad (26\text{-}112)$$

This solution is implicit in mass flux G_{*p}. To illustrate its application, first consider the special case of horizontal pipe flow. The term η_{sp} is defined as follows for both horizontal and inclined pipe flow.

HEM for Horizontal Pipe Discharge For horizontal pipe flow, $F_I = q = 0$, and:

$$I_o(\eta) = \frac{-1}{\frac{1}{2}b + c\eta} \quad (26\text{-}113)$$

The general compressible flow solution simplifies for horizontal pipe flow to:

$$G_{*p}^2 = 2\,\frac{\left\{(\eta_1 - \eta_{sp}) + \dfrac{(\eta_{sp} - \eta_2)}{1-\omega} + \dfrac{\omega\eta_s}{(1-\omega)^2} \ln\left[\dfrac{\varepsilon_2\eta_2}{\varepsilon_{sp}\eta_{sp}}\right]\right\}}{N + 2\ln\left[\dfrac{\varepsilon_2}{\varepsilon_{sp}}\right]} \quad (26\text{-}114)$$

The solution is again generalized with the term η_{sp} and $\varepsilon_{sp} = \varepsilon(\eta_{sp})$. For Regimes 1 and 2, $\alpha_o = 0$, so $\omega = \omega_s$. Regime 2 is again split, depending on where the flashing occurs, in the orifice or in the line. The division between low and moderate subcooling is found by:

$$\eta_{st} = \frac{2\omega_s}{1 + 2\omega_s + N} \quad (26\text{-}115)$$

Regime 1 is included in the following two subcases of Regime 2:

- For the low subcooling case, which includes Regime 1, $\eta_s > \eta_{st}$ and $\eta_s > \eta_1$ (flashing occurs in the vessel or pipe entrance). Set $\eta_{sp} = \eta_1$.
- For the moderate subcooling case, $\eta_s > \eta_{st} > \eta_2$ (flashing occurs in the pipe). Set $\eta_{sp} = \eta_s$.
- For the high subcooling case, $\eta_s < \eta_{st}$, use the single-phase orifice equation, Eq. (26-104).

For Regime 3, $\omega = \alpha_o$, and the integration is developed letting $\eta_s = 1$, so the above solution applies with $\eta_{sp} = 1$.

The solution of these equations requires a root-finding algorithm which iterates on assumed values of η_1. At each value of η_1, solve Eq. (26-95) (with η_1 replacing η_2) for G_{*ori}. Find η_2 from Eq. (26-101), subject also to:

$$\eta_2 \geq \eta_a$$

Solve Eq. (26-114) for G_{*p}. The function:

$$f(\eta_1) = G_{*ori} - G_{*p} \quad (26\text{-}116)$$

always has a root in the interval $1 < \eta_1 < \eta_a$ since G_{*ori} increases with decreasing η_1 and G_{*p} decreases with decreasing η_1.

The maximum value for G_{*p} is G_{*ori} evaluated with zero pipe length. Denoting this value as G_{*max}, Fig. 26-68 plots the dimensionless mass

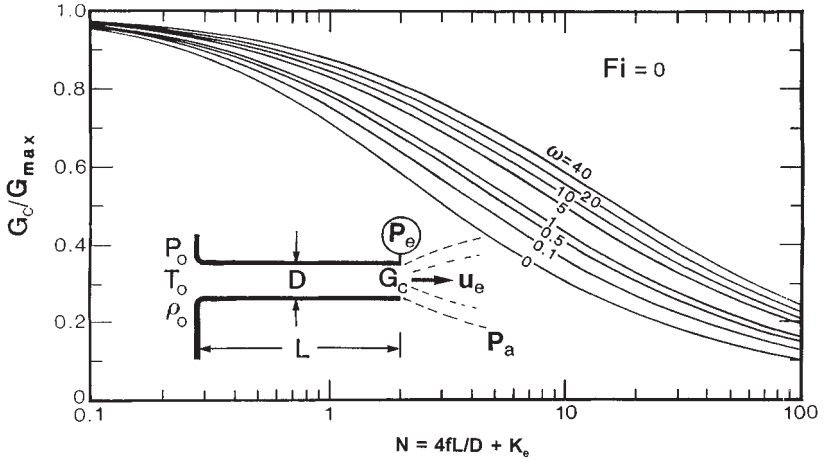


FIG. 26-68 Ratio of mass flux for horizontal pipe flow to that for orifice discharge for flashing liquids by the homogeneous equilibrium model. (*Leung and Grolmes,* AIChE J, **33** *(3), pp. 524–527, 1987; reproduced by permission of AIChE. copyright 1987. All rights reserved.)*

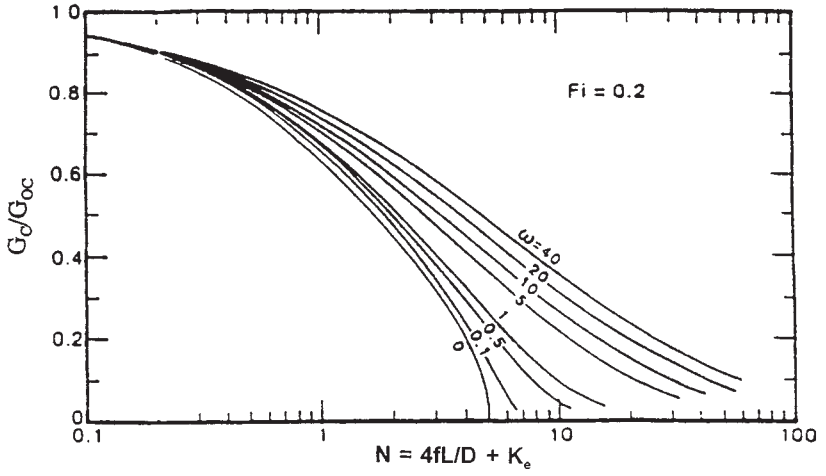


FIG. 26-69 Ratio of mass flux for inclined pipe flow to that for orifice discharge for flashing liquids by the homogeneous equilibrium model. (*Leung, J. of Loss Prev. Process Ind.* ***3*** *pp. 27–32, with kind permission of Elsevier Science, Ltd, The Boulevard, Langford Lane, Kidlington, OX5 1GB U.K., 1990.*)

flux discharge for horizontal pipe flow $G_{\circ p}$ as a ratio $G_{\circ p}/G_{\circ \max}$. Similar design charts were developed by Levenspiel (1977).

Figure 26-69 plots $G_{\circ p}/G_{\circ \max}$ for an upwardly inclined pipe flow [Eq. (26-105)] for a specific value of the pipe inclination factor F_I = 0.2. Comparing Figs. 26-68 and 26-69 shows that discharge rates decrease with upflow. For downflow, the curves are higher than in horizontal flow. In fact, a minimum flow occurs, regardless of how much pipe length is added, quite similar to the terminal velocity of free-falling objects. These charts are useful for design calculations up to a reduced temperature (ratio of temperature to the critical temperature) of about 0.90.

Accuracy of Omega Method HEM Figures 26-70 and 26-71 illustrate the accuracy to be expected with the omega method HEM. For slightly subcooled (flashing) or saturated water, using the data of Sozzi and Sutherland (1975) and the ASME Symposium on Non-Equilibrium Two-Phase Flows (1975), predictions improve to within 10 percent error when the pipe length is larger than about 0.5 m.

NEM for Two-Phase Orifice Discharge With flow through an orifice or nozzle, the flash is delayed, and the delay time depends on the initial concentration of nucleation sites for vaporization. A simplified approach to represent nonequilibrium orifice or nozzle flow has been suggested by Henry and Fauske ("The Two-Phase Critical Flow of One-Component Mixtures in Nozzles, Orifices, and Short Tubes," *Trans. ASME, J. Heat Transfer* **93**(5): 179–N87, 1976) and by Chisholm (1983).

For orifice flow, Eq. (26-80) reduces to:

$$-vdP = G^2 v dv \tag{26-117}$$

or, differentiating the definition of *G:*

$$-vdP = udu = \frac{1}{2}du^2 \tag{26-118}$$

This can be readily integrated numerically as long as we use the appropriate nonequilibrium equivalent specific volume v_e in the integration. A reasonably simple form for v_e has been suggested by Chisholm (1983), which makes use of established correlations for the slip velocity *K,* which depends on the Lockhart-Martinelli parameter *X.* Integrating Eq. (26-118) gives:

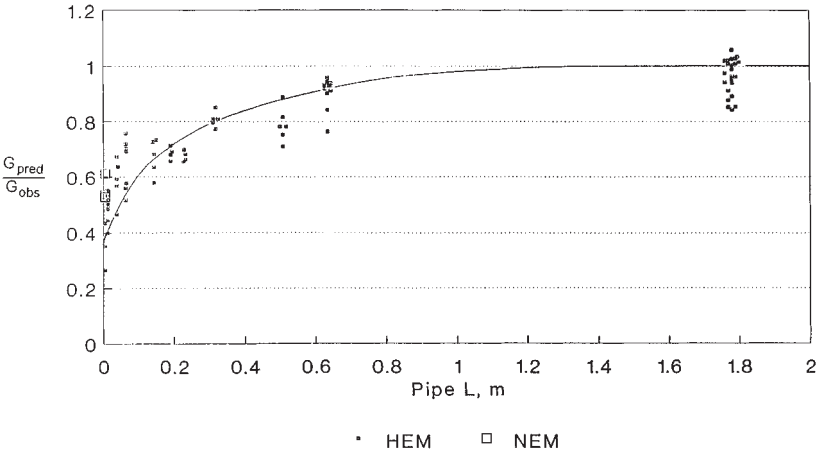


FIG. 26-70 Accuracy in HEM predictions for slightly to moderately subcooled flashing flow. Comparison with data for water by Sozzi and Sutherland (1975); also ASME Symposium on Non-Equilibrium Two-Phase Flows (1975) (Nozzle type 2).

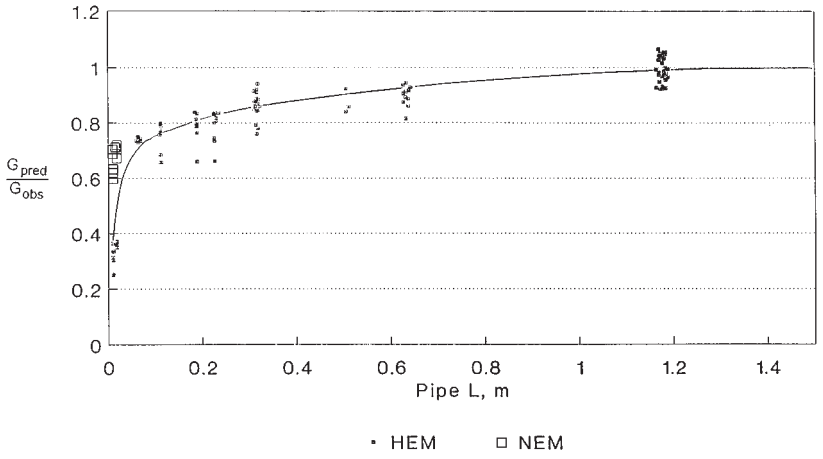


FIG. 26-71 Accuracy in HEM predictions for saturated, flashing flow. Comparison with data for water by Sozzi and Sutherland (1975), (Nozzle type 2).

$$-\int_{P_o}^{P_2} v\,dP = u_2^2\left[1-\left(\frac{u_o}{u_2}\right)^2\right] \tag{26-119}$$

Making use of continuity:

$$w = A_o\frac{u_o}{v_o} = A_2\frac{u_2}{v_2} \tag{26-120}$$

Equation (26-119) can be rearranged and written in dimensionless variables as:

$$G_{\circ 2}^2 = \frac{-2\int_1^{\eta_2}\varepsilon_e\,d\eta}{\varepsilon_{e2}^2\left[1-\left(\frac{A_2\varepsilon_{e1}}{A_1\varepsilon_{e2}}\right)^2\right]} = \frac{-2\int_1^{\eta_2}\varepsilon_e\,d\eta}{\varepsilon_{e2}^2 - C_D^2} \tag{26-121}$$

since $C_D = A_2/A_o$ at the vena contracta, $G_{\circ 2} = G_{\circ C}$. Equation (26-131) gives $G_{\circ ori}$.

The integral of Eq. (26-121) is evaluated in increments of pressure ratio $d\eta$, using the following procedure. At the next pressure given by:

$$P_i = P_{i-1} - \Delta\eta P_o \tag{26-122}$$

use an equation of state to find v_G, v_L. Use an isentropic flash to find the equilibrium flash fraction x. The initial vapor mass fraction x_o can include noncondensables as well as an initial flash fraction. If this is the case, add the noncondensable portion to x.

Find the Lockhart-Martinelli coefficient as defined by Lockhart and Martinelli (1949):

$$X_m^2 = \frac{dP_L}{dP_G} = \frac{f_L(1-x)^2}{f_G x^2}\frac{v_L}{v_G} \tag{26-123}$$

or the ratio of the pressure drop for liquid flowing alone to that for gas flowing alone. The liquid and gas friction factors are usually justifiably taken as equal (unless one phase is in laminar flow while the other is in turbulent).

Find the equilibrium, homogeneous specific volume v_H given by Eq. (26-85) and estimate the slip velocity ratio using the following correlation:

$$K_o = \begin{cases}\left[\frac{v_H}{v_L}\right]^{1/2} & \text{if } X_m > 1\\ \left[\frac{v_G}{v_L}\right]^{1/4} & \text{if } X_m < 1\end{cases} \tag{26-124}$$

The slip velocity ratio is adequately represented by:

$$K = \frac{u_G}{u_L} = K_o^{0.4} \tag{26-125}$$

Find the coefficient in the equivalent specific volume B using:

$$B = \frac{(1/K)\,(v_G/v_L) + K - 2}{(v_G/v_L) - 1} \tag{26-126}$$

or, if

$$\frac{v_G}{v_L} >> K\,(K-2)$$

$$B = \frac{1}{K} \tag{26-127}$$

Find the transition flash fraction x_t:

$$x_t = \frac{1}{1+(v_G/v_L)^{1/2}} \tag{26-128}$$

The nonequilibrium flash fraction x_N is interpolated nonlinearly between x_o and x_t by:

$$x_N = \begin{cases} x_o + \left(\frac{x-x_o}{x_t-x_o}\right)^2 (x-x_o) & x < x_t\\ x & x > x_t\end{cases} \tag{26-129}$$

So when $x > x_t$, thermal equilibrium is assumed.

Find the equivalent nonequilibrium specific volume as:

$$\varepsilon_e = \frac{v_e}{v_o} = 1 + \left(\frac{v_G}{v_L} - 1\right)[Bx_N(1-x_N) + x_N^2] \tag{26-130}$$

The integration proceeds stepwise until the integral begins to decrease. This occurs at the choked pressure ratio η_c, giving a maximum mass flux $G_{\circ 2c}$.

As shown in Figs. 26-70 and 26-71, the orifice flow predictions by the NEM (open points) are larger than those of the HEM, although still low compared with these particular data.

Discharge Coefficients and Gas Discharge A compressible fluid, upon discharge from an orifice, accelerates from the puncture point and the cross-sectional area contracts until it forms a minimum at the vena contracta. If flow is choked, the mass flux $G_{\circ c}$ can be found at the vena contracta, since it is a maximum at that point. The mass flux at the orifice is related to the mass flux at the vena contracta by the discharge coefficient, which is the area contraction ratio (A_c at the vena contracta to A_N at the orifice):

$$G_{\circ ori} = C_D G_{\circ c} \tag{26-131}$$

For two-phase flow, the phase contraction coefficients C_{DG} and C_{DL} relate the area of each phase A_G and A_L at the vena contracta to the known area of the orifice A_N. Thus:

$$C_{DG} = \frac{A_G}{A_N}, \qquad C_{DL} = \frac{A_L}{A_N} \tag{26-132}$$

The two-phase discharge coefficient is:

$$C_D = \frac{A_G + A_L}{A_N} = \frac{xv_G + K(1-x)v_L}{\dfrac{xv_G}{C_{DG}} + \dfrac{K(1-x)v_L}{C_{DL}}} \tag{26-133}$$

where K is the slip velocity ratio, u_G/u_L given by Eq. (26-125). The contraction coefficient for liquids is generally accepted as $C_{DL} = 0.61$. For the gas phase, as developed by Jobson (1955):

$$C_{DG} = \frac{1}{2b_1\eta_{2c}^{1/k}}\left\{a_1 - \left[a_1^2 - \frac{4\eta_{2c}^{2/k}(1-\eta_2)b_1}{G_{*g}^2}\right]^{1/2}\right\} \tag{26-134}$$

$$b_1 = \frac{1}{C_{DL}} - \frac{1}{2C_{DL}^2} \tag{26-135}$$

$$a_1 = 1 + \frac{(\eta_{2c} - \eta_2)\eta_{2c}^{1/k}}{G_{*g}^2} \tag{26-136}$$

where: $$G_{*g}^2 = \frac{2k}{(k-1)}\eta_2^{2/k}(1 - \eta_2^{(k-1)/k}) \tag{26-137}$$

and for vapor or gas flow:

$$G_{*ori} = C_{DG}\, G_{*g} \tag{26-138}$$

Equation (26-137) is recognized as the expression for all-gas flow by adiabatic expansion across an orifice or nozzle. The factor k is the expansion coefficient for the adiabatic flow equation of state:

$$\frac{P}{P_o} = \left[\frac{\rho}{\rho_o}\right]^k = \left[\frac{T}{T_o}\right]^{k/(k-1)} \tag{26-139}$$

For an ideal gas:

$$k = \frac{C_p}{C_v} \tag{26-140}$$

Fortunately, for most operating pressure ranges, k is nearly constant with temperature and pressure. For wider ranges where this might not hold it is often adequate to replace k by a value slightly smaller than C_p/C_v. A rationale for this is that heat exchange with the surroundings can shift the behavior slightly toward the isothermal solution, which is a limiting case with $k = 1$.

TABLE 26-30 Variation in Two-Phase Discharge Coefficients by Jobson Equations

Exit pressure ratio, η_2	$\frac{C_{DG}}{C_{DL}}$	C_{DG}
1.0	1.0	0.61
0.8	1.07	0.653
0.6	1.18	0.720
0.4	1.31	0.799
0.2	1.40	0.854
0.0	1.44	0.878

A further generalization for two-phase flow as suggested by Tangren et al. (1949) is to use the generalized value of k as:

$$k = \frac{xC_{pG} + (1-x)C_{PL}}{xC_{vG} + (1-x)C_{PL}} \tag{26-141}$$

For gas-phase choked flow, the pressure ratio at the vena contracta is:

$$\eta_{2c} = \left(\frac{2}{k+1}\right)^{k/(k-1)} \tag{26-142}$$

and $$\eta_2 = \text{maximum}(\eta_{2c}, \eta_a)$$

reaching η_a when the flow becomes subsonic.

For choked flow, $a_1 = 1$ in Eq. (26-136). Typical values developed by Eqs. (26-133) and (26-134) are listed in Table 26-30 (Watson et al., 1983).

Blowdown Modeling Blowdown models incorporate not only the preceding discharge rate models but also a model of the tank and line contents to predict how the tank pressure and temperature decay in time. Analytical time-varying blowdown solutions are available for single-phase discharge, gas or liquid (Woodward and Mudan, 1991). Analytical liquid blowdown models have been developed for essentially all tank geometries of interest by Sommerfeld and coworkers (Lee and Sommerfeld, May 1994, July 1994). Vapor blowdown is readily modeled, using an energy and mass balance on the tank contents. The tank pressure decays along the vapor pressure curve as long as a liquid is present. Two-phase blowdown modeling is further discussed in Woodward (1993, pp. 94–159).

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Nomenclature and Units

Symbol	Definition	SI units	U.S. customary units
A	Area specific resistance	Ω/m^2	Ω/ft^2
c	Heat capacity	J/(kg·K)	Btu/(lb·°F)
E	Activation energy	J/mol	Btu/lb mol
E	Electrical potential	V	V
$\hat{f}$	Fugacity	kPa	psia
F	Faraday constant	C/mol	C/lb mol
ΔG	Free energy of reaction	J/mol	Btu/lb mol
ΔH	Heat of reaction	J/mol	Btu/lb mol
i	Current density	A/m^2	A/ft^2
k	Rate constant	$g/(h\cdot cm^3)$	$lb/(h\cdot ft^3)$
K	Latent heat of vaporization	kJ/kg	Btu/lb
P	Pressure	kPa	psia
Q	Heating value	kJ/kg	Btu/lb
R	Gas constant	J/mol·K	Btu/lb mol·°R
s	Relative density	Dimensionless	Dimensionless
T	Temperature	K	°F
U	Fuel utilization	percent	percent
V	Molar gas volume	m^3/mol	ft^3/lb mol
Z	Compressibility factor	Dimensionless	Dimensionless
	Greek symbols		
ε	Energy conversion efficiency	Percent	Percent

Acronyms and unit prefixes

Symbol	Name	Value
E	Exa	10^{18}
G	Giga	10^9
K	Kilo	10^3
M	Mega	10^6
P	Peta	10^{15}
T	Tera	10^{12}
Z	Zetta	10^{21}

Acronym	Definition
AFBC	atmospheric fluidized bed combustion
AFC	alkaline fuel cell
AGC-21	Advanced Gas Conversion Process
BG/L	British Gas and Lurgi process
COE	cost of electricity
COED	Char Oil Energy Development Process
DOE	U.S. Department of Energy
EDS	Exxon Donor Solvent Process
FBC	fluidized bed combustion
HAO	hydrogenated anthracene oil
HPO	hydrogenated phenanthrene oil
HRI	Hydrocarbon Research, Inc.
HTI	Hydrocarbon Technologies, Inc.
IGCC	integrated gasification combined-cycle
KRW	Kellogg-Rust-Westinghouse process
MCFC	molten carbonate fuel cell
MTG	methanol-to-gasoline process
OTFT	once-through-Fischer-Tropsch process
PAFC	phosphoric acid fuel cell
PC	pulverized coal
PEFC	polymer electrolyte fuel cell
PFBC	pressurized fluidized bed combustion
Quad	10^{15} Btu
SASOL	South African operation of synthetic fuels plants
SMDS	Shell Middle Distillate Synthesis Process
SNG	synthetic natural gas
SOFC	solid oxide fuel cell
SRC	solvent-refined coal

INTRODUCTION

General References: Loftness, *Energy Handbook,* 2d ed., Van Nostrand Reinhold, New York, 1984. Energy Information Administration, *Energy Use and Carbon Emissions: Some International Comparisons,* U.S. Dept. of Energy, DOE/EIA-0579, 1994. Howes and Fainberg (eds.), *The Energy Source Book,* American Institute of Physics, New York, 1991. Johansson, Kelly, Reddy, and Williams (eds.), Burnham (exec. ed.), *Renewable Energy—Sources for Fuels and Electricity,* Island Press, Washington, D.C., 1993. Turner, *Energy Management Handbook,* The Fairmont Press, Lilburn, Ga., 1993. *National Energy Strategy,* U.S. Dept. of Energy, 1991.

Energy is usually defined as the capacity to do work. Nature provides us with numerous sources of energy, some difficult to utilize efficiently (e.g., solar radiation and wind energy), others more concentrated or energy dense and therefore easier to utilize (e.g., fossil fuels). Energy sources can be classified also as *renewable* (solar and nonsolar) and *nonrenewable.* Renewable energy resources are derived in a number of ways: gravitational forces of the sun and moon, which create the tides; the rotation of the earth combined with solar energy, which generates the currents in the ocean and the winds; the decay of radioactive minerals and the interior heat of the earth, which provide geothermal energy; photosynthetic production of organic matter; and the direct heat of the sun. These energy sources are called renewable because they are either continuously replenished or, for all practical purposes, are inexhaustible.

Nonrenewable energy sources include the fossil fuels (natural gas, petroleum, shale oil, coal, and peat) as well as uranium. Fossil fuels are both energy dense and widespread, and much of the world's industrial, utility, and transportation sectors rely on the energy contained in them. Concerns over global warming notwithstanding, fossil fuels will remain the dominant fuel form for the foreseeable future. This is so for two reasons: (1) the development and deployment of new technologies able to utilize renewable energy sources such as solar, wind, and biomass are uneconomic at present, in most part owing to the diffuse or intermittent nature of the sources; and (2) concerns persist over storage and/or disposal of spent nuclear fuel and nuclear proliferation.

Fossil fuels, therefore, remain the focus of this section; their principal use is in the generation of heat and electricity in the industrial, utility, and commercial sectors, and in the generation of shaft power in transportation. The material in this section deals primarily with the conversion of the chemical energy contained in fossil fuels to heat and electricity. Material from *Perry's Chemical Engineers' Handbook,* 6th ed., Sec. 9, has been updated and condensed, and, in addition, new material on electrochemical energy conversion in fuel cells has been introduced. Even though the principles of energy conversion in fuel cells were known before internal combustion engines were developed, only recent improvements in materials and manufacturing methods have allowed fuel cells to be considered for stationary and transportation power generation.

FUELS

RESOURCES AND RESERVES

Proven worldwide energy resources are large. The largest remaining known reserves of crude oil, used mainly for producing transportation fuels, are located in the Middle East, along the equator, and in the former Soviet Union. U.S. proven oil reserves currently account for only about 3 percent of the world's total. Large reserves of natural gas exist in the former Soviet Union and the Middle East. Coal is the most abundant fuel on earth and the primary fuel for electricity in the United States, which has the largest proven reserves. Annual world consumption of energy is still currently less than 1 percent of combined world reserves of fossil fuels. The resources and reserves of the principal fossil fuels in the United States—coal, petroleum, and natural gas—follow.

	ZJ*		
Fuel	Proven reserves	Estimated undiscovered recoverable reserves	Estimated identified and undiscovered resources
Coal	7.3		110
Petroleum	0.15	0.31	
Natural gas	0.19	0.43	

*ZJ = 10^{21} J. (To convert to 10^{18} Btu, multiply by 0.948.)

The energy content of fossil fuels in commonly measured quantities is as follows.

Energy content		
Bituminous and anthracite coal	30.2 MJ/kg	26×10^6 Btu/US ton
Lignite and subbituminous coal	23.2 MJ/kg	20×10^6 Btu/US ton
Crude oil	38.5 MJ/L	5.8×10^6 Btu/bbl
Natural-gas liquids	25.2 MJ/L	3.8×10^6 Btu/bbl
Natural gas	38.4 MJ/m^3	1032 Btu/ft^3

1 bbl = 42 US gal = 159 L = 0.159 m^3

SOLID FUELS

Coal

General References: Lowry (ed.), *Chemistry of Coal Utilization,* Wiley, New York, 1945; suppl. vol., 1963; 2d suppl. vol., Elliott (ed.), 1981. Van Krevelen, *Coal,* Elsevier, Amsterdam, 1961.

Origin Coal originated from the arrested decay of the remains of trees, bushes, ferns, mosses, vines, and other forms of plant life, which flourished in huge swamps and bogs many millions of years ago during prolonged periods of humid, tropical climate and abundant rainfall. The precursor of coal was peat, which was formed by bacterial and chemical action on the plant debris. Subsequent actions of heat, pressure, and other physical phenomena metamorphosed the peat to the various ranks of coal as we know them today. Because of the various degrees of the metamorphic changes during this process, coal is not a uniform substance; no two coals are ever the same in every respect.

Classification Coals are classified by rank, i.e., according to the degree of metamorphism in the series from lignite to anthracite. Table 27-1 shows the classification system adopted by the American Society for Testing and Materials, D388-92A. The heating value on the moist *mineral-matter-free* (mmf) basis, and the fixed carbon, on the dry mmf basis, are the bases of this system. The lower-rank coals are classified according to the heating value, kJ/kg (Btu/lb), on a moist mmf basis. The agglomerating character is used to differentiate between adjacent groups. Coals are considered agglomerating if the coke button remaining from the test for volatile matter will support a weight of 500 g or if the button swells or has a porous cell structure.

The Parr formulas, Eqs. (27-1) to (27-3), or the approximation formulas, Eqs. (27-4) and (27-5), are used for classifying coals according to rank. The Parr formulas are employed in litigation cases.

$$F' = \frac{100\,(F - 0.15S)}{100 - (M + 1.08A + 0.55S)} \tag{27-1}$$

$$V' = 100 - F' \tag{27-2}$$

TABLE 27-1 Classification of Coals by Rank*

	Fixed carbon limits (dry, mineral-matter-free basis), %		Volatile matter limits (dry, mineral-matter-free basis), %		Gross calorific value limits (moist, mineral-matter-free basis)†				
					MJ/kg		Btu/lb		
Class/group	Equal or greater than	Less than	Greater than	Equal or less than	Equal or greater than	Less than	Equal or greater than	Less than	Agglomerating character
Anthracitic:									
Meta-anthracite	98	—	—	2	—	—	—	—	
Anthracite	92	98	2	8	—	—	—	—	Nonagglomerating
Semianthracite‡	86	92	8	14	—	—	—	—	
Bituminous:									
Low-volatile bituminous coal	78	86	14	22	—	—	—	—	
Medium-volatile bituminous coal	69	78	22	31	—	—	—	—	
High-volatile A bituminous coal	—	69	31	—	32.6	—	14,000§	—	Commonly agglomerating¶
High-volatile B bituminous coal	—	—	—	—	30.2	32.6	13,000§	14,000	
High-volatile C bituminous coal	—	—	—	—	26.7	30.2	11,500	13,000	
					24.4	26.7	10,500	11,500	Agglomerating
Subbituminous:									
Subbituminous A coal	—	—	—	—	24.4	26.7	10,500	11,500	
Subbituminous B coal	—	—	—	—	22.1	24.4	9,500	10,500	
Subbituminous C coal	—	—	—	—	19.3	22.1	8,300	9,500	Nonagglomerating
Lignitic:									
Lignite A	—	—	—	—	14.7	19.3	6,300	8,300	
Lignite B	—	—	—	—	—	14.7	—	6,300	

Data from 1994 Annual Book of ASTM Standards, vol. 5 D 388 (1994). Copyright ASTM. Reprinted with permission.
*This classification does not apply to certain coals.
†*Moist* refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.
‡If agglomerating, classify in low-volatile group of the bituminous class.
§Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of gross calorific value.
¶It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class and that there are notable exceptions in the high-volatile C bituminous group.

$$Q' = \frac{100\,(Q - 50S)}{100 - (M + 1.08A + 0.55S)} \tag{27-3}$$

$$F' = \frac{100F}{100 - (M + 1.1A + 0.1S)} \tag{27-4}$$

$$Q' = \frac{100Q}{100 - (1.1A + 0.1S)} \tag{27-5}$$

where M, F, A, and S are weight percentages, on a moist basis, of moisture, fixed carbon, ash, and sulfur, respectively; F' and V' are weight percentages, on a dry mmf basis, of fixed carbon and volatile matter, respectively; Q and Q' are calorific values (Btu/lb), on a moist nonmmf basis and a moist mmf basis, respectively. (Btu/lb = 2326 J/kg)

Composition and Heating Value The composition of coal is reported in two different ways: the proximate analysis and the ultimate analysis, both expressed in weight percent. The *proximate analysis* is the determination by prescribed methods of moisture, volatile matter, fixed carbon, and ash.

The moisture in coal consists of inherent moisture, also called equilibrium moisture, and surface moisture. Free moisture is that moisture lost when coal is air-dried under standard low-temperature conditions.

The *volatile matter* is the portion of coal which, when the coal is heated in the absence of air under prescribed conditions, is liberated as gases and vapors. Volatile matter does not exist by itself in coal, except for a little absorbed methane, but results from thermal decomposition of the coal substance.

Fixed carbon, the residue left after the volatile matter is driven off, is calculated by subtracting from 100 the percentages of moisture, volatile matter, and ash of the proximate analysis. In addition to carbon, it may contain several tenths of a percent of hydrogen and oxygen, 0.4 to 1.0 percent nitrogen, and about half of the sulfur that was in the coal.

Ash is the inorganic residue that remains after the coal has been burned under specified conditions, and it is composed largely of compounds of silicon, aluminum, iron, and calcium, and minor amounts of compounds of magnesium, sodium, potassium, phosphorous, sulfur, and titanium. Ash may vary considerably from the original mineral matter, which is largely kaolinite, illite, montmorillonite, quartz, pyrites, and gypsum.

The *ultimate analysis* is the determination by prescribed methods of the ash, carbon, hydrogen, nitrogen, sulfur, and (by difference) oxygen. Along with these analyses, the *heating value,* expressed as kJ/kg (Btu/lb), is also determined. This is the heat produced at constant volume by the complete combustion of a unit quantity of coal in an oxygen-bomb calorimeter under specified conditions. The result includes the latent heat of vaporization of the water in the combustion products and is called the gross heating or *high heating value* (HHV), Q_h. The heating value when the water is not condensed is called the *low heating value* (LHV), Q_l, and is obtained from

$$Q_l = Q_h - K \cdot W \tag{27-6}$$

where W = weight of water formed/weight of fuel burned. The factor K is the latent heat of vaporization at the partial pressure of the vapor in the exit gas. The value of K ranges from 2396 to 2512 kJ/kg of water (1030 to 1080 Btu/lb). Q_h in Btu/lb (×2.326 = kJ/kg) can be approximated by a formula developed by the Institute of Gas Technology:

$$Q_h = 146.58\,C + 568.78\,H + 29.4\,S - 6.58\,A - 51.53\,(O + N) \tag{27-7}$$

where C, H, S, A, O, and N are the weight percentages on a dry basis of carbon, hydrogen, sulfur, ash, oxygen, and nitrogen, respectively. The standard deviation for 775 coal samples is 127 Btu/lb.

Coal analyses are reported on several bases, and it is customary to select the basis best suited to the application. The *as-received* basis represents the weight percentage of each constituent in the sample as received in the laboratory. The sample itself may be coal as fired, as mined, or as prepared for a particular use. The *moisture-free* (dry) basis is generally the most useful basis because performance calculations can be easily corrected for the actual moisture content at the point of use. The *dry, ash-free* basis is frequently used to approximate the rank and source of a coal. For example, the heating value of coals of a given source and rank is remarkably constant when calculated on this basis.

Laboratory procedures for proximate and ultimate analyses are given in the *Annual Book of ASTM Standards* (Sec. 5, American Society for Testing and Materials, Conshohocken, Pa., 1994) and in *Methods of Analyzing and Testing Coal and Coke* (U.S. Bureau of Mines Bulletin 638, 1967).

Sulfur Efforts to abate atmospheric pollution have drawn considerable attention to the sulfur content of coal, since the combustion of coal results in the discharge to the atmosphere of sulfur oxides. Sulfur occurs in coal in three forms: as pyrite (FeS_2); as organic sulfur, which is a part of the coal substance; and as sulfate. Sulfur as sulfate comprises at the most only a few hundredths of a percent of the coal. The organic sulfur may comprise from 20 to 80 percent of the total sulfur. Since organic sulfur is chemically bound to the coal substance in a complex manner, drastic treatment is necessary to break the chemical bonds before the sulfur can be removed. There is no economical method known at present that will remove organic sulfur, although so-called chemical treatment methods for cleaning coal can reduce the sulfur content. Pyritic sulfur can be partially removed by using standard coal-washing equipment. The degree of pyrite removal depends on the size of the coal and the size and distribution of the pyrite particles.

The sulfur content of U.S. coals varies widely, ranging from a low of 0.2 percent to as much as 7 percent by weight, on a dry basis. The estimated remaining U.S. coal reserves of all ranks, by sulfur content, are shown in Fig. 27-1. Extensive data on sulfur and sulfur reduction potential, including washability, in U.S. coals are given in *Sulfur and Ash Reduction Potential and Selected Chemical and Physical Properties of United States Coal* (U.S. Dept. of Energy, DOE/PETC, TR-90/7, 1990; TR-91/1 and TR-91/2, 1991).

Coal-Ash Characteristics and Composition When coal is to be burned, used in steelmaking, or gasified, it is important to determine the ash fusibility, comprising the initial deformation, softening, and fluid temperatures. The difference between the softening and initial deformation temperatures is called the *softening interval,* and that between the fluid temperature and the softening temperature is called the *fluid interval.* The procedure for determining the fusibility of coal ash is prescribed by ASTM D 1857 (American Society for Testing and Materials, op. cit., 1994). The softening temperature is most

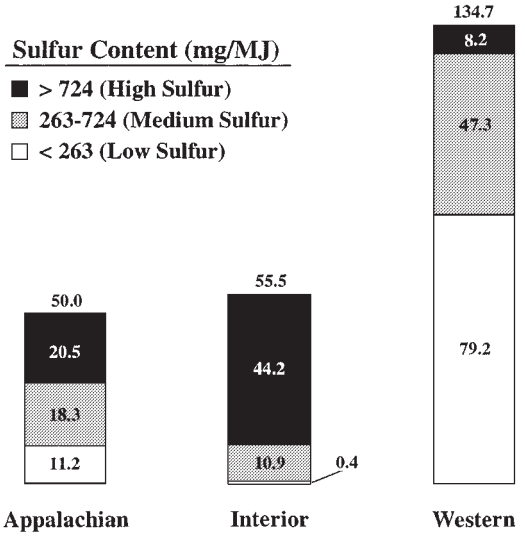


FIG. 27-1 Estimates of recoverable U.S. coal reserves in Gt by sulfur ranges and region. To convert tonnes to US tons, multiply by 1.102; and mg/MJ to lb/10^{16} Btu, multiply by 2.321. (*Source:* U.S. Coal Reserves: An Update by Heat and Sulfur Content, *Energy Information Administration, DOE/EIA-0529(92), February 1993.*)

often used as a rough qualitative guide to the behavior of ash on a grate and on furnace heat-transfer surfaces, with respect to the tendency to form large masses of sintered or fused ash, which impair heat transfer and impede gas flow. Likewise, the fluid temperature and the fluid interval are qualitative guides to the "flowability" of ash in slag-tap and cyclone furnaces. However, because ash fusibility is not an infallible index of ash behavior in practice, care is needed in using fusibility data for designing and operating purposes. There is an excellent discussion on this subject in *Steam: Its Generation and Use* (40th ed., Babcock & Wilcox Co., New York, 1992).

The composition of coal ash varies widely. Calculated as oxides, the composition (percent by weight) varies as follows:

SiO_2	20–60
Al_2O_3	10–35
Fe_2O_3	5–35
CaO	1–20
MgO	0.3–4
TiO_2	0.5–2.5
Na_2O and K_2O	1–4
SO_3	0.1–12

Knowledge of the composition of coal ash is useful for estimating and predicting coal performance in coke making and, to a limited extent, the fouling and corrosion of heat-exchange surfaces in pulverized-coal-fired furnaces.

Multiple correlations for ash composition and ash fusibility are discussed in the *Coal Conversion Systems Technical Data Book* (part IA, U.S. Dept. of Energy, 1984).

The slag viscosity-temperature relationship for completely melted slag is

$$\text{Log viscosity} = \frac{10^7 M}{(T - 150)^2 + C} \qquad (27\text{-}8)$$

where viscosity is in poises ($\times 0.1$ = Pa·s), M = 0.00835 (SiO_2) + 0.00601(Al_2O_3) − 0.109, C = 0.0415 (SiO_2) + 0.0192 (Al_2O_3) + 0.0276 (equivalent Fe_2O_3) + 0.0160 (CaO) − 3.92, and T = temperature, K.

The oxides in parentheses are the weight percentages of these oxides when $SiO_2 + Al_2O_3 + Fe_2O_3 + CaO + MgO = 100$.

Physical Properties The *free-swelling index* (FSI) measures the tendency of a coal to swell when burned or gasified in fixed or fluidized beds. Coals with a high FSI (greater than 4) can usually be expected to cause difficulties in such beds. Details of the test are given by the ASTM D 720 (American Society for Testing and Materials, op. cit.) and U.S. Bureau of Mines Report of Investigations 3989.

The *Hardgrove grindability index* (HGI) indicates the ease (or difficulty) of grinding coal and is complexly related to physical properties such as hardness, fracture, and tensile strength. The Hardgrove machine is usually employed (ASTM D 409, American Society for Testing and Materials, op. cit.). It determines the relative grindability or ease of pulverizing coal in comparison with a standard coal, chosen as 100 grindability (see Sec. 20 of this handbook). The FSI and HGI of some U.S. coals are given in Bureau of Mines Information Circular 8025 for FSI and HGI data for 2812 and 2339 samples, respectively.

The *bulk density* of broken coal varies according to the specific gravity, size distribution, and moisture content of the coal and the amount of settling when the coal is piled. Following are some useful approximations of the bulk density of various ranks of coal.

	kg/m³	lb/ft³
Anthracite	800–930	50–58
Bituminous	670–910	42–57
Lignite	640–860	40–54

Size stability refers to the ability of coal to withstand breakage during handling and shipping. It is determined by twice dropping a 23-kg (50-lb) sample of coal from a height of 1.8 m (6 ft) onto a steel plate. From the size distribution before and after the test, the size stability is reported as a percentage factor (see ASTM D 440). The *friability* test measures the tendency of coal to break during repeated handling. It is actually the complement of size stability and is determined by the standard tumbler test (ASTM D 441-36).

Spier's *Technical Data on Fuels* gives the *specific heat* of dry, ash-free coal as follows.

	kJ/(kg·K)	Btu/(lb·°F)
Anthracite	0.92–0.96	0.22–0.23
Bituminous	1.0–1.1	0.24–0.25

The relationships between specific heat and water content and between specific heat and ash content are linear. Given the specific heat on a dry, ash-free basis, it can be corrected to an as-received basis. The specific heat and enthalpy of coal to 1366 K (2000°F) are given in *Coal Conversion Systems Technical Data Book* (part 1A, U.S. Dept. of Energy, 1984).

The *mean specific heat* of coal ash and slag, which is used for calculating heat balances on furnaces, gasifiers, and other coal-consuming systems, follows.

Temperature range		Mean specific heat	
K	°F	kJ/(kg·K)	Btu/(lb·°F)
273–311	32–100	0.89	0.21
273–1090	32–1500	0.94	0.22
273–1310	32–1900	0.97	0.23
273–1370	32–2000	0.98	0.24
273–1640	32–2500	1.1	0.27

Coke Coke is the solid, cellular, infusible material remaining after the carbonization of coal, pitch, petroleum residues, and certain other carbonaceous materials. The varieties of coke generally are identified by prefixing a word to indicate the source, if other than coal, (e.g., *petroleum* coke) or the process by which a coke is manufactured (e.g., *oven* coke).

The mechanism of the formation of coke when coal is carbonized is a complex of physical and chemical phenomena that are not perfectly understood. Some of the physical changes, which are interrelated when certain ranks of coal or blends are heated, are softening, devolatilization, swelling, and resolidification. Some of the accompanying chemical changes are cracking, depolymerization, polymerization, and condensation. More detailed theoretical information is given in the general references listed in the beginning of the section on coal.

High-Temperature Coke (1173 to 1423 K or 1652 to 2102°F.) This type is most commonly used in the United States; nearly 20 percent of the total bituminous coal consumed is used to make high-temperature coke for metallurgical applications. About 99 percent of this type of coke is made in slot-type recovery ovens. Blast furnaces use about 90 percent of the production, the rest going mainly to foundries and gas plants.

A U.S. Bureau of Mines survey of 12 blast-furnace coke plants, whose capacity is 30 percent of the total production in the United States, provides an excellent picture of the acceptable chemical and physical properties of metallurgical coke. The ranges of properties are given in Table 27-2.

TABLE 27-2 Chemical and Physical Properties of High-Temperature Cokes Used in the United States*

Property	Range
Volatile matter	0.6–1.4 wt %, as received
Ash	7.5–10.7 wt %, as received
Sulfur	0.6–1.1 wt %, as received
Stability factor	39–58 (1-in tumbler)
Hardness factor	60–68 (¼-in tumbler)
Apparent specific gravity (water = 1.0)	0.80–0.99

**Comparison of Properties of Coke Produced by BM-AGA and Industrial Methods,* U.S. Bur. Mines Rep. Invest. 6354. To convert inches to centimeters, multiply by 2.54.

The typical by-product yields per US ton (909 kg) of dry coal from high-temperature carbonization in ovens with inner-wall temperatures from 1273 to 1423 K (1832 to 2102°F) are: coke, 653 kg (1437 lb); gas, 154 kg (11,200 ft^3); tar, 44 kg (10 gal); water, 38 kg (10 gal); light oil, 11 kg (3.3 gal); and ammonia, 2.2 kg (4.8 lb).

Foundry Coke This coke has different requirements from blast-furnace coke. The volatile matter should not exceed 2.0 percent, the sulfur should not exceed 0.7 percent, the ash should not exceed 12.0 percent, and the size should exceed 76 mm (3 in).

Low- and Medium-Temperature Coke (773 to 1023 K or 932 to 1382°F.) Cokes of this type are no longer produced in the United States to a significant extent. However, there is some interest in low-temperature carbonization as a source of both hydrocarbon liquids and gases to supplement petroleum and natural-gas resources.

The *Fischer assay* is an arbitrary but precise analytical tool for determining the yield of products from low-temperature carbonization. A known weight of coal is heated at a controlled rate in the absence of air to 773 K (932°F), and the products are collected and weighed. Table 27-3 gives the approximate yields of products for various ranks of coal.

Pitch Coke and Petroleum Coke Pitch coke is made from coal-tar pitch, and petroleum coke is made from petroleum residues from petroleum refining. Pitch coke has about 1.0 percent volatile matter, 1.0 percent ash, and less than 0.5 percent sulfur on the as-received basis. There are two kinds of petroleum coke: delayed coke and fluid coke. Delayed coke is produced by heating a gas oil or heavier feedstock to 755 to 811 K (900 to 1000°F) and spraying it into a large vertical cylinder where cracking and polymerization reactions occur. Water jets are used to cut the coke from one drum while the other drum is being charged. Fluid coke is made in a fluidized-bed reactor where preheated feed is sprayed onto a fluidized bed of coke particles. Coke product is continuously withdrawn by size classifiers in the solids loop of the reactor system. Since it contains the impurities from the original crude oil, the sulfur is usually high, and appreciable quantities of vanadium salts may be present. Ranges of composition and properties are as follows.

Composition and properties	Delayed coke	Fluid coke
Volatile matter, wt %	8–18	3.7–7.0
Ash, wt %	0.05–1.6	0.1–2.8
Sulfur, wt %	—	1.5–10.0
Grindability index	40–60	20–30
True density, g/cm^3	1.28–1.42	1.5–1.6

Other Solid Fuels

Coal Char This type of char is the nonagglomerated, nonfusible residue from the thermal treatment of coal. Coal chars are obtained as a residue or a coproduct from low-temperature carbonization processes and from processes being developed to convert coal to liquid and gaseous fuels and to chemicals. Such chars have a substantial heating value. The net amount of char from a conversion process varies widely; in some instances, it may represent between about 30 and 55 percent of the weight of the coal feed; in others, no net or excess char is produced; i.e., the entire char yield is consumed as in-plant fuel. The volatile matter, sulfur, and heating values of the chars are lower, and the ash is higher, than in the original coal. Chars typically have higher volatile matter contents (7 to 12 wt %) than low- and medium-temperature cokes (2.5 to 6 wt %), but this is both process and feed-coal dependent.

Peat Peat is partially decomposed plant matter that has accumulated underwater or in a water-saturated environment. It is the precursor of coal but is not classified as coal. Sold under the term *peat moss* or *moss peat*, peat is used in the United States mainly for horticultural and agricultural applications, but interest is growing in its use as a fuel in certain local areas (e.g., North Carolina). Peat is used extensively as a fuel primarily in Ireland and the former Soviet Union. Although analyses of peat vary widely, a typical high-grade peat has 90 percent water, 3 percent fixed carbon, 5 percent volatile matter, 1.5 percent ash, and 0.10 percent sulfur. The moisture-free heating value is approximately 20.9 MJ/kg (9000 Btu/lb).

Wood Typical higher heating values are 20 MJ/kg (8600 Btu/lb) for oven-dried hardwood and 20.9 MJ/kg for oven-dried softwood. These values are accurate enough for most engineering purposes. U.S. Department of Agriculture Handbook 72 (revised 1974) gives the specific gravity of the important softwoods and hardwoods, useful if heating value on a volume basis is needed.

Charcoal Charcoal is the residue from the destructive distillation of wood. It absorbs moisture readily, often containing as much as 10 to 15 percent water. In addition, it usually contains about 2 to 3 percent ash and 0.5 to 1.0 percent hydrogen. The heating value of charcoal is about 27,912 to 30,238 kJ/kg (12,000 to 13,000 Btu/lb).

Solid Wastes and Biomass Large and increasing quantities of solid wastes are a significant feature of affluent societies. In the United States in 1993 the rate was about 1.8 kg (4 lb) per capita per day or nearly 190 Tg (2.07×10^8 U.S. tons) per year, but the growth rate has slowed in recent years as recycling efforts have increased. Table 27-4 shows that the composition of miscellaneous refuse is surprisingly uniform, but size and moisture variations cause major difficulties in efficient, economical disposal.

The fuel value of most solid wastes is usually sufficient to enable self-supporting combustion, leaving only the incombustible residue and reducing the volume of waste eventually consigned to sanitary landfills to only 10 to 15 percent of the original volume. The heat released by the combustion of waste can be recovered and utilized, although the cost of the recovery equipment or the distance to a suitable point of use for the heat may make its recovery economically infeasible.

Wood, wood scraps, bark, and wood product plant waste streams are a major element of biomass, industrial, and municipal solid waste fuels. In 1991, about 1.7 EJ (1.6×10^{15} Btu [quads]) of energy were obtained from wood and wood wastes, representing about 60 percent of the total biomass-derived energy in the United States. *Bagasse* is the solid residue remaining after sugarcane has been crushed by pressure rolls. It usually contains from 40 to 50 percent water. The dry bagasse has a heating value of 18.6 to 20.9 MJ/kg (8000 to 9000 Btu/lb).

TABLE 27-3 Fischer-Assay Yields from Various Ranks of Coal (As-Received Basis)

ASTM classification by rank		Coke, wt %	Tar, gal/ton	Light oil, gal/ton	Gas, ft^3/ton	Water, wt %
Class	Group					
Bituminous	1. Low-volatile bituminous	90	8.6	1.0	1760	3
	2. Medium-volatile bituminous	83	18.9	1.7	1940	4
	3. High-volatile A bituminous	76	30.9	2.3	1970	6
	4. High-volatile B bituminous	70	30.3	2.2	2010	11
	5. High-volatile C bituminous	67	27.0	1.9	1800	16
Subbituminous	1. Subbituminous A	59	20.5	1.7	2660	23
	2. Subbituminous B	58	15.4	1.3	2260	28
Lignite	1. Lignite A	37	15.2	1.2	2100	44

NOTE: To convert gallons per ton to liters per kilogram, multiply by 0.004; to convert cubic feet per ton to cubic meters per kilogram, multiply by 3.1×10^{-5}.

TABLE 27-4 Waste Fuel Analysis

Type of waste	Heating value, Btu/lb	Percentage composition by weight					Density, lb/ft^3
		Volatiles	Moisture	Ash	Sulfur	Dry combustible	
Paper	7,572	84.6	10.2	6.0	0.20		
Wood	8,613	84.9	20.0	1.0	0.05		
Rags	7,652	93.6	10.0	2.5	0.13		
Garbage	8,484	53.3	72.0	16.0	0.52		
Coated fabric: rubber	10,996	81.2	1.04	21.2	0.79	78.80	23.9
Coated felt: vinyl	11,054	80.87	1.50	11.39	0.80	88.61	10.7
Coated fabric: vinyl	8,899	81.06	1.48	6.33	0.02	93.67	10.1
Polyethylene film	19,161	99.02	0.15	1.49	0	98.51	5.7
Foam: scrap	12,283	75.73	9.72	25.30	1.41	74.70	9.1
Tape: resin-covered glass	7,907	15.08	0.51	56.73	0.02	43.27	9.5
Fabric: nylon	13,202	100.00	1.72	0.13	0	99.87	6.4
Vinyl scrap	11,428	75.06	0.56	4.56	0.02	95.44	23.4

SOURCE: From Hescheles, *MECAR Conference on Waste Disposal,* New York, 1968; and *Refuse Collection Practice,* 3d ed., American Public Works Association, Chicago, 1966.

To convert British thermal units per pound to joules per kilogram, multiply by 2326; to convert pounds per cubic foot to kilograms per cubic meter, multiply by 16.02.

LIQUID FUELS

Liquid Petroleum Fuels The principal liquid fuels are made by fractional distillation of crude petroleum (a mixture of hydrocarbons and hydrocarbon derivatives ranging from methane to heavy bitumen). As many as one-quarter to one-half of the molecules in crude may contain sulfur atoms, and some contain nitrogen, oxygen, vanadium, nickel, or arsenic. Desulfurization, hydrogenation, cracking (to lower molecular weight), and other refining processes may be performed on selected fractions before they are blended and marketed as fuels. Viscosity/gravity/boiling-range relationships of common fuels are shown in Fig. 27-2.

Specifications The American Society for Testing and Materials has developed specifications (*Annual Book of ASTM Standards*, Conshohocken, Pa., updated annually) that are widely used to classify fuels. Table 27-5 shows fuels covered by ASTM D 396, Standard Specification for Fuel Oils. D 396 omits kerosenes (low-sulfur, clean-burning No. 1 fuels for lamps and freestanding flueless domestic heaters), which are covered separately by ASTM D 3699.

In drawing contracts and making acceptance tests, refer to the pertinent ASTM standards. *ASTM Standards* contain specifications (classifications) and test methods for burner fuels (D 396), motor and aviation gasolines (D 4814 and D 910), diesel fuels (D 975), and aviation and gas-turbine fuels (D 1655 and D 2880). ASTM D 4057 contains procedures for sampling bulk oil in tanks, barges, etc.

Fuel specifications from different sources may differ in test limits on sulfur, density, etc., but the same general categories are recognized worldwide: kerosene-type vaporizing fuel, distillate (or "gas oil") for atomizing burners, and more viscous blends and residuals for commerce and heavy industry. Typical specifications are as follows.

Specifier	Number	Category
Canadian Government Specification Board, Department of Defense Production, Ottawa, Canada	3-GP-2	Fuel oil, heating
Deutschen Normenauschusses, Berlin 15	DIN 51603	Heating (fuel) oils
British Standards Institution, British Standards House, 2 Park Street, London, WIA 2BS	B.S. 2869	Petroleum fuels for oil engines and burners
Japan	JIS K2203 JIS K2204 JIS K2205	Kerosene Gas oil Fuel oils
Federal specifications, United States	ASTM D 396	Fuel oil, burner

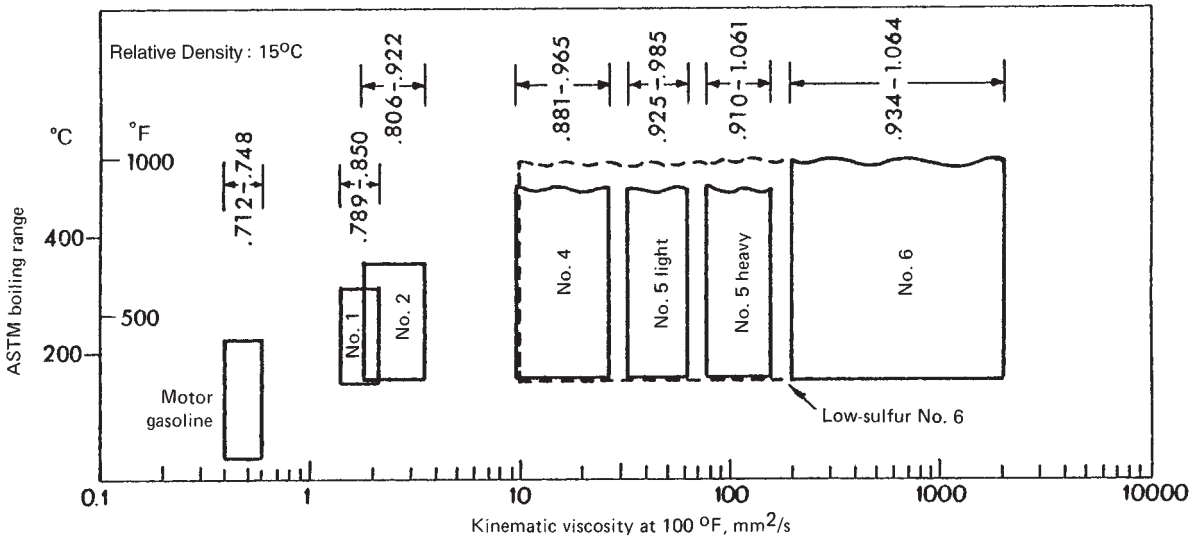


FIG. 27-2 Viscosity, boiling-range, and gravity relationships for petroleum fuels.

TABLE 27-5 Detailed Requirements for Fuel Oils[a]

Property	ASTM test method[b]	No. 1	No. 2	Grade No. 4 (light)	No. 4	No. 5 (light)	No. 5 (heavy)	No. 6
Flash point, °C, min.	D 93	38	38	38	55	55	55	60
Water and sediment, % vol. max.	D 1796	0.05	0.05	(0.50)[c]	(0.50)[c]	(1.00)[c]	(1.00)[c]	(2.00)[c]
Distillation temperature, °C	D 86							
10% vol. recovered, max.		215	—	—	—	—	—	—
90% vol. recovered, min.			282	—	—	—	—	—
max.		288	338	—	—	—	—	—
Kinematic viscosity at 40°C (104°F), mm^2/s	D 445	—	—	—	—	—	—	—
min.		1.3	1.9	1.9	>5.5	—	—	—
max.		2.1	3.4	5.5	24.0[d]	—	—	—
Kinematic viscosity at 100°C (212°F), mm^2/s								
min.	—	—	—	—	—	5.0	9.0	15.0
max.	—	—	—	—	—	8.9[d]	14.9[d]	50.0[d]
Ramsbottom carbon residue on 10% distillation residue, % mass, max.	D 524	0.15	0.35	—	—	—	—	—
Ash, % mass, max.	D 482	—	—	0.05	0.10	0.15	0.15	—
Sulfur, % mass max[e]	D 129	0.50	0.50	—	—	—	—	—
Copper strip corrosion rating, max., 3 h at 50°C	D 130	No. 3	No. 3	—	—	—	—	—
Density at 15°C, kg/m^3	D 1298							
min.		—	—	>876[f]	—	—	—	—
max.		850	876	—	—	—	—	—
Pour point °C, max[g]	D 97	−18	−6	6	−6	—	—	[h]

[a] Source ASTM D 396-92. It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade. However, to meet special operating conditions modifications of individual limiting requirements may be agreed upon among the purchaser, seller, and manufacturer. Copyright ASTM. Reprinted with permission.

[b] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in Section 2 and 5.1.

[c] The amount of water by distillation by Test Method D 95 plus the sediment by extraction by Test Method D 473 shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.5 mass % and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass %.

[d] Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower-numbered grade down to and including No. 4 can be supplied by agreement between the purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

[e] Other sulfur limits may apply in selected areas in the United States and in other countries.

[f] This limit assures a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

[g] Lower or higher pour points can be specified whenever required by conditions of storage or use. When a pour point less than −18°C is specified, the minimum viscosity at 40°C for grade No. 2 shall be 1.7 mm^2/s and the minimum 90% recovered temperature shall be waived. (Add 273 to °C to obtain K.)

[h] Where low sulfur fuel oil is required, Grade No. 6 fuel oil will be classified as *low pour* (+15°C max.) or *high pour* (no max.). Low-pour fuel oil should be used unless tanks and lines are heated.

Foreign specifications are generally available from the American National Standards Institute, New York; United States federal specifications, at Naval Publications and Forms, Philadelphia.

Equipment manufacturers and large-volume users often write fuel specifications to suit particular equipment, operating conditions, and economics. Nonstandard test procedures and restrictive test limits should be avoided; they reduce the availability of fuel and increase its cost.

Bunker-fuel specifications for merchant vessels are described by ASTM D 2069, Standard Specification for Marine Fuels. Deep draft vessels carry residual (e.g., No. 6 fuel oil) or distillate-residual blend for main propulsion, plus distillate for start-up, shutdown, maneuvering, deck engines, and diesel generators. Main-propulsion fuel is identified principally by its viscosity in centistokes at 373 K. Obsolete designations include those based on Redwood No. 1 seconds at 100°F (311 K) (e.g., "MD 1500") and the designations "Bunker A" for No. 5 fuel oil and "Bunker B" and "Bunker C" for No. 6 fuel oil in the lower- and upper-viscosity ranges, respectively.

Chemical and Physical Properties Petroleum fuels contain paraffins, isoparaffins, naphthenes, and aromatics, plus organic sulfur, oxygen, and nitrogen compounds that were not removed by refining. Olefins are absent or negligible except when created by severe refining. Vacuum-tower distillate with a final boiling point equivalent to 730 to 840 K (850 to 1050°F) at atmospheric pressure may contain from 0.1 to 0.5 ppm vanadium and nickel, but these metal-bearing compounds do not distill into No. 1 and 2 fuel oils.

Black, viscous residuum directly from the still at 410 K (390°F) or higher serves as fuel in nearby furnaces or may be cooled and blended to make commercial fuels. Diluted with 5 to 20 percent distillate, the blend is No. 6 fuel oil. With 20 to 50 percent distillate, it becomes No. 4 and No. 5 fuel oils for commercial use, as in schools and apartment houses. Distillate-residual blends also serve as diesel fuel in large stationary and marine engines. However, distillates with inadequate solvent power will precipitate asphaltenes and other high-molecular-weight colloids from *visbroken* (severely heated) residuals. A blotter test, ASTM D 4740, will detect sludge in pilot blends. Tests employing centrifuges, filtration (D 4870), and microscopic examination have also been used.

No. 6 fuel oil contains from 10 to 500 ppm vanadium and nickel in complex organic molecules, principally porphyrins. These cannot be removed economically, except incidentally during severe hydrodesulfurization (Amero, Silver, and Yanik, *Hydrodesulfurized Residual Oils as Gas Turbine Fuels,* ASME Pap. 75-WA/GT-8). Salt, sand, rust, and dirt may also be present, giving No. 6 a typical ash content of 0.01 to 0.5 percent by weight.

Ultimate analyses of some typical fuels are shown in Table 27-6.

The hydrogen content of petroleum fuels can be calculated from density with the following formula, with an accuracy of about 1 percent for petroleum liquids that contain no sulfur, water, or ash:

$$H = 26 - 15s \tag{27-9}$$

where H = percent hydrogen and s = relative density at 15°C (with respect to water), also referred to as specific gravity. Schmidt (*Fuel Oil Manual,* 3d ed., Industrial Press, New York, 1969) claims improved precision of the formula by replacing 26 with different constants.

Relative density (288 K)	API gravity	Constant
1.0754–1.0065	0–9	24.50
1.0065–0.9935	10–20	25.00
0.9935–0.8757	21–30	25.20
0.8757–0.8013	31–45	25.45

Relative density is usually determined at ambient temperature with specialized hydrometers. In the United States these hydrometers commonly are graduated in an arbitrary scale termed *degrees API.* This scale relates inversely to relative density s (at 60°F) as follows (see also the abscissa scale of Fig. 27-3):

TABLE 27-6 Typical Ultimate Analyses of Petroleum Fuels

Composition, %	No. 1 fuel oil (41.5° A.P.I.)	No. 2 fuel oil (33° A.P.I.)	No. 4 fuel oil (23.2° A.P.I.)	Low sulfur, No. 6 F.O. (12.6° A.P.I.)	High sulfur, No. 6 (15.5° A.P.I.)
Carbon	86.4	87.3	86.47	87.26	84.67
Hydrogen	13.6	12.6	11.65	10.49	11.02
Oxygen	0.01	0.04	0.27	0.64	0.38
Nitrogen	0.003	0.006	0.24	0.28	0.18
Sulfur	0.09	0.22	1.35	0.84	3.97
Ash	<0.01	<0.01	0.02	0.04	0.02
C/H Ratio	6.35	6.93	7.42	8.31	7.62

NOTE: The C/H ratio is a weight ratio.

$$\text{Degrees API} = \frac{141.5}{s} - 131.5 \qquad (27\text{-}10)$$

For practical engineering purposes, relative density at 15°C (288 K), widely used in countries outside the United States, is considered equivalent to specific gravity at 60°F (288.6 K). With the adoption of SI units, the American Petroleum Institute favors absolute density at 288 K instead of degrees API.

The hydrogen content, heat of combustion, specific heat, and thermal conductivity data herein were abstracted from Bureau of Standards Miscellaneous Publication 97, *Thermal Properties of Petroleum Products.* These data are widely used, although other correlations have appeared, notably that by Linden and Othmer (*Chem. Eng.* **54**[4, 5], April and May, 1947).

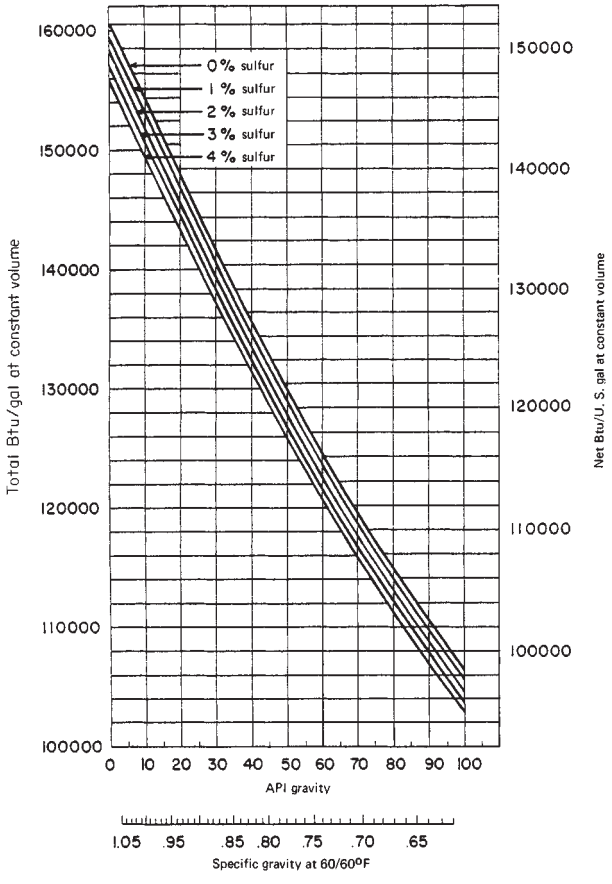


FIG. 27-3 Heat of combustion of petroleum fuels. To convert Btu/US gal to kJ/m^3, multiply by 278.7.

Heat of combustion can be estimated within 1 percent from the relative density of the fuel by using Fig. 27-3. Corrections for water and sediment must be applied for residual fuels, but they are insignificant for clean distillates.

Pour point ranges from 213 K (–80°F) for some kerosene-type jet fuels to 319 K (115°F) for waxy No. 6 fuel oils. *Cloud point* (which is not measured on opaque fuels) is typically 3 to 8 K higher than pour point unless the pour has been depressed by additives. Typical petroleum fuels are practically newtonian liquids between the cloud point and the boiling point and at pressures below 6.9 MPa (1000 psia).

Fuel systems for No. 1 (kerosene) and No. 2 fuel oil (diesel, home heating oil) are not heated. Systems for No. 6 fuel oil are usually designed to preheat the fuel to 300 to 320 K (90 to 120°F) to reduce viscosity for handling and to 350 to 370 K (165 to 200°F) to reduce viscosity further for proper atomization. No. 5 fuel oil may also be heated, but preheating is usually not required for No. 4. (See Table 27-5.) Steam or electric heating is employed as dictated by economics, climatic conditions, length of storage time, and frequency of use. Pressure relief arrangements are recommended on sections of heated pipelines when fuel could be inadvertently trapped between valves.

The *kinematic viscosity* of a typical No. 6 fuel oil declines from 5000 mm^2/s (0.054 ft^2/s) at 298 K (77°F) to about 700 mm^2/s (0.0075 ft^2/s) and 50 mm^2/s (0.000538 ft^2/s) on heating to 323 K (122°F) and 373 K (212°F), respectively. Viscosity of 1000 mm^2/s or less is required for manageable pumping. Proper boiler atomization requires a viscosity between 15 and 65 mm^2/s.

Thermal expansion of petroleum fuels can be estimated as volume change per unit volume per degree. ASTM-IP Petroleum Measurement Tables (ASTM D 1250 IP 200) are used for volume corrections in commercial transactions.

Heat capacity (specific heat) of petroleum liquids between 0 and 205°C (32 and 400°F), having a relative density of 0.75 to 0.96 at 15°C (60°F), can be calculated within 2 to 4 percent of the experimental values from the following equations:

$$c = \frac{1.685 + (0.039 \times °\text{C})}{\sqrt{s}} \qquad (27\text{-}11)$$

$$c' = \frac{0.388 + (0.00045 \times °\text{F})}{\sqrt{s}} \qquad (27\text{-}12)$$

where c is heat capacity, kJ/(kg·°C) or kJ/(kg·K), and c' is heat capacity, Btu/(lb·°F). Heat capacity varies with temperature, and the arithmetic average of the values at the initial and final temperatures can be used for calculations relating to the heating or cooling of oil.

The *thermal conductivity* of liquid petroleum products is given in Fig. 27-4. Thermal conductivities for asphalt and paraffin wax in their solid states are 0.17 and 0.23 W/(m·K), respectively, for temperatures above 273 K (32°F) (1.2 and 1.6 Btu/[h·ft^2][°F/in]).

Commercial Considerations Fuels are sold in gallons and in multiples of the 42-gal barrel (0.159 m^3) in the United States, while a weight basis is used in other parts of the world. Transactions exceeding about 20 to 40 m^3 (5000 to 10,000 US gal) usually involve volume corrections to 288 K (60°F) for accounting purposes. Fuel passes through an air eliminator and mechanical meter when loaded into or dispensed from trucks. Larger transfers such as pipeline, barge, or tanker movements are measured by fuel depth and *strapping tables* (calibration tables) in tanks and vessels, but positive-displacement

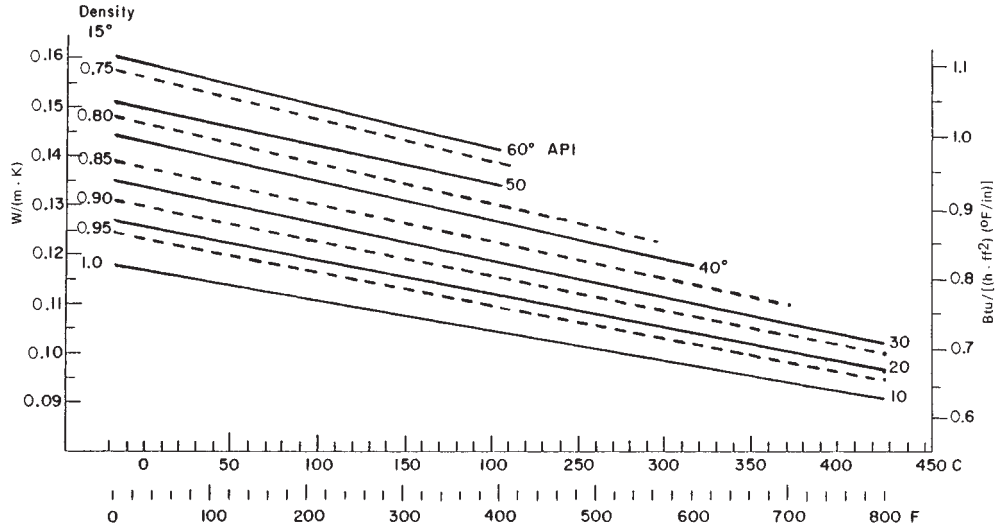


FIG. 27-4 Thermal conductivity of petroleum liquids. The solid lines refer to density expressed as degrees API; the broken lines refer to relative density at 288 K (15°C). (K = [°F + 459.7]/1.8)

meters that are *proved* (calibrated) frequently are gaining acceptance. After an appropriate settling period, water in the tank bottom is measured with a plumb bob or stick smeared with water-detecting paste.

Receipts of tank-car quantities or larger are usually checked for gravity, appearance, and flash point to confirm product identification and absence of contamination.

Safety Considerations Design and location of storage tanks, vents, piping, and connections are specified by state fire marshals, underwriters codes, and local ordinances. In NFPA 30, *Flammable and Combustible Liquids Code, 1993* (published by the National Fire Protection Association, Quincy, Mass.), liquid petroleum fuels are classified as follows for safety in handling:

Class I (flammable) liquid has a flash point below 311 K (100°F) and a vapor pressure not exceeding 0.28 MPa at 311 K (40 psia at 100°F).

Class IA includes those liquids having flash points below 296 K (73°F) and boiling points below 311 K (100°F).

Class IB liquids have flash points below 296 K (73°F) and boiling points at or above 311 K (100°F).

Class IC includes those liquids having flash points at or above 296 K (73°F) and below 311 K (100°F).

Class II combustible liquids have flash points at or above 311 K (100°F) and below 333 K (140°F).

Class IIIA combustible liquids have flash points at or above 333 K (140°F) and below 366 K (200°F).

Class IIIB liquids flash at or above 366 K (200°F).

NFPA 30 details the design features and safe placement of handling equipment for flammable and combustible liquids.

Crude oils with flash points below 311 K (100°F) have been used in place of No. 6 fuel oil. Different pumps may be required because of low fuel viscosity.

Nonpetroleum Liquid Fuels

Tar Sands Canadian tar sands are strip-mined and extracted with hot water to recover heavy oil (bitumen). The oil is processed into naphtha, kerosene, and gasoline fractions (which are hydrotreated), in addition to gas (which is recovered). Tar sands are being developed in Utah also.

Oil Shale Oil shale is nonporous rock containing organic kerogen. Raw shale oil is extracted from mined rock by pyrolysis in a surface retort, or in situ by steam injection after breaking up the rock with explosives. Pyrolysis cracks the kerogen, yielding raw shale oil high in nitrogen, oxygen, and sulfur. *Shale oil* has been hydrotreated and refined in demonstration tests into relatively conventional fuels. Refining in petroleum facilities is possible, and blending with petroleum is most likely.

Coal-Derived Fuels Liquid fuels derived from coal range from highly aromatic coal tars to liquids resembling petroleum. Raw liquids from different hydrogenation processes show variations that reflect the degree of hydrogenation achieved. Also, the raw liquids can be further hydrogenated to refined products. Properties and cost depend on the degree of hydrogenation and the boiling range of the fraction selected. A proper balance between fuel upgrading and equipment modification is essential for the most economical use of coal liquids in boilers, industrial furnaces, diesels, and stationary gas turbines.

Coal-tar fuels are high-boiling fractions of crude tar from pyrolysis in coke ovens and coal retorts. Grades range from free-flowing liquids to pulverizable pitch. Low in sulfur and ash, they contain hydrocarbons, phenols, and heterocyclic nitrogen and oxygen compounds. Being more aromatic than petroleum fuels, they burn with a more luminous flame. From 288 to 477 K (60 to 400°F) properties include:

Heat capacity	1.47–1.67 kJ/(kg·K) (0.35–0.40 Btu/[lb·°F])
Thermal conductivity	0.14–0.15 W/(m·K) (0.080–0.085 Btu/[h·ft·°F])
Heat of vaporization	349 kJ/kg (150 Btu/lb)
Heat of fusion	Nil

Table 27-7 shows representative data for liquid fuels from tar sands, oil shale, and coal.

GASEOUS FUELS

Natural Gas Natural gas is a combustible gas that occurs in porous rock of the earth's crust and is found with or near accumulations of crude oil. It may occur alone in separate reservoirs, but more commonly it forms a gas cap entrapped between petroleum and an impervious, capping rock layer in a petroleum reservoir. Under high-pressure conditions, it is mixed with or dissolved in crude oil. Natural gas termed *dry* has less than 0.013 dm^3/m^3 (0.1 gal/1000 ft^3) of gasoline. Above this amount, it is termed *wet*.

The proven reserves of natural gas in the United States total about 4.58 Tm^3 (1.62×10^{14} ft^3). Production in 1993 was about 0.51 Tm^3 (1.8×10^{13} ft^3). Revisions and adjustments to the existing resource base, together with modest new additions to proven reserves, have held the recent decline in reserves to about 1.6 percent per year.

Natural gas consists of hydrocarbons with a very low boiling point.

TABLE 27-7 Characteristics of Typical Nonpetroleum Fuels

	Conventional coal-tar fuels from retorting[a]		Typical coal-derived fuels with different levels of hydrogenation[b]					Synthetic crude oils, by hydrogenation	
	CTF 50	CTF 400	Minimal		Mild	Mild[c]	Severe	Oil shale	Tar sands[d]
Distillation range, °C			175–280	280–500	160–415	175–400	125–495		
Density, kg/m³, 15°C	1.018	1.234	0.974	1.072	0.964	0.9607	0.914	0.817	0.864
lb U.S. gal, 60°F	8.5	10.3	8.1	8.9	8.0	8.0	7.6	6.8	7.2
Viscosity, mm²/s	2–9	9–18	3.1–3.4	50–90	3.6	—	2.18		
	At 38°C	At 121°C	At 38°C	At 38°C	At 38°C	—	At 38°C		
Ultimate analysis, %									
Carbon	87.4	90.1	86.0	89.1	87.8	89.6	89.0	86.1	87.1
Hydrogen	7.9	5.4	9.1	7.5	9.7	10.1	11.1	13.84	12.69
Oxygen	3.6	2.4	3.6–4.3	1.4–1.8	2.4	0.3	0.5	0.12	0.04
Nitrogen	0.9	1.4	0.9–1.1	1.2–1.4	0.6	0.04	0.09	0.01	0.07
Sulfur	0.2	0.7	<0.2	0.4–0.5	0.07	0.004	0.04	0.02	0.10
Ash[e]	Trace	0.15	<0.001	[f]					
C/H ratio, weight	11.0	16.5	9.4	11.9	9.1	8.9	8.0	6.2	6.9
Gross calorific value, MJ/kg	38.4–40.7	36.8–37.9							
Btu/lb	16,500–17,500	15,800–16,300							

[a] CTF 50 and 400 indicate approximate preheat temperature, °F, for atomization of fuel in burners (terminology used in British Standard B.S. 1469).
[b] Properties depend on distillation range, as shown, and to a lesser extent on coal source.
[c] Using recycle-solvent process.
[d] Tar sands, although a form of petroleum, are included in this table for comparison.
[e] Inorganic mineral constituents of coal tar fuel:
5 to 50 ppm: Ca, Fe, Pb, Zn (Na, in tar treated with soda ash)
0.05 to 5 ppm: Al, Bi, Cu, Mg, Mn, K, Si, Na, Sn
Less than 0.05 ppm: As, B, Cr, Ge, Ti, V, Mo
Not detected: Sb, Ba, Be, Cd, Co, Ni, Sr, W, Zr
[f] Inherent ash is "trace" or "<0.1%," although entrainment in distillation has given values as high as 0.03 to 0.1%.

Methane is the main constituent, with a boiling point of 119 K (–245°F). Ethane, with a boiling point of 184 K (–128°F) may be present in amounts up to 10 percent; propane, with a boiling point of 231 K (–44°F), up to 3 percent. Butane, pentane, hexane, heptane, and octane may also be present. Physical properties of these hydrocarbons are given in Sec. 2.

Although there is no single composition that may be called "typical" natural gas, Table 27-8 shows the range of compositions in large cities in the United States.

Most natural gas is substantially free of sulfur compounds; the terms *sweet* and *sour* are used to denote the absence or presence of H_2S. Some wells, however, deliver gas containing levels of hydrogen sulfide and other sulfur compounds (e.g., thiophenes, mercaptans, and organic sulfides) that must be removed before transfer to commercial pipelines. Pipeline-company contracts typically specify maximum allowable limits of impurities; H_2S and total sulfur compounds seldom exceed 0.023 and 0.46 g/m³ (1.0 and 20.0 gr/100 std ft³), respectively. The majority of pipeline companies responding to a 1994 survey limited H_2S to less than 0.007 g/m³ (0.3 gr/100 std ft³), but a slightly smaller number continued specifying 0.023 g/m³, in accord with an American Gas Association 1971 recommendation.

TABLE 27-8 Analysis of Natural Gas*

	Range†	
	Low	High
Composition, vol %		
Methane	86.3	95.2
Ethane	2.5	8.1
Propane	0.6	2.8
Butanes	0.13	0.66
Pentanes	0	0.44
Hexanes plus	0	0.09
CO_2	0	1.1
N_2	0.31	2.47
He	0.01	0.06
Heating value MJ/m³ (Btu/ft³)	38.15(1024)	40.72(1093)
Specific gravity Ref.: Air at 288 K (60°F)	0.586	0.641

*Adapted from *Gas Engineers Handbook,* American Gas Association, Industrial Press, New York, 1965.
†Ranges are the high and low values of annual averages reported by 13 utilities (1954 data).

Compressibility of Natural Gas All gases deviate from the perfect gas law at some combinations of temperature and pressure, the extent depending on the gas. This behavior is described by a dimensionless compressibility factor Z that corrects the perfect gas law for real-gas behavior, $PV = ZRT$. Any consistent units may be used. Z is unity for an ideal gas, but for a real gas, Z has values ranging from less than 1 to greater than 1, depending on temperature and pressure. The compressibility factor is described further in Secs. 2 and 4 of this handbook.

Because the value of Z for natural gas is significantly less than unity at ambient temperatures and at pressures greater than 1 MPa (145 psia), the compressibility must be taken into account in gas measurement: gas purchased at high line pressure will give a greater volume when the pressure is reduced than it would if the gas were ideal. Natural gas pipeline operators use a *supercompressibility* factor, also called Z, but defined as

$$Z = \left(\frac{RT}{PV}\right)^{1/2} \tag{27-13}$$

which is convenient for use with differential pressure flowmeters but sometimes a source of confusion. For determining compressibility factors of natural-gas mixtures, see *Manual for the Determination of Supercompressibility Factors for Natural Gas*, American Gas Association, New York, 1963; and A.G.A Gas Measurement Committee Report No. 3, 1969.

Liquefied Natural Gas The advantages of storing and shipping natural gas in liquefied form (LNG) derive from the fact that 0.035 m³ (1 ft³) of liquid methane at 111 K (–260°F) equals about 18 m³ (630 ft³) of gaseous methane. Temperatures higher than 111 K can be used if the liquid is stored under pressure. For example, the liquid state is maintained at 2.24 MPa (325 psia) and 170 K (–155°F). The critical temperature of methane is 191 K (–160°F), and the corresponding critical pressure is 4.64 MPa (673 psia). One cubic meter (264 US gal) weighs 412 kg (910 lb) at 109 K (–263°F). The heating value is about 24 GJ/m³ (86,000 Btu/US gal).

The heat of vaporization of LNG at 0.1 MPa (1 bar) is 232 MJ/m³

(832 Btu/US gal) of liquid. On a product gas basis, the heat required is about 0.3 kJ/m^3 (10 Btu/std ft^3) of gas produced.

LNG is stored in metal double-wall or prestressed concrete tanks, frozen earth, or mined quarries or caverns.

Liquefied Petroleum Gas The term *liquefied petroleum gas* (LPG) is applied to certain specific hydrocarbons which can be liquefied under moderate pressure at normal temperatures but are gaseous under normal atmospheric conditions. The chief constituents of LPG are propane, propylene, butane, butylene, and isobutane. LPG produced in the separation of heavier hydrocarbons from natural gas is mainly of the paraffinic (saturated) series. LPG derived from oil-refinery gas may contain varying low amounts of olefinic (unsaturated) hydrocarbons.

LPG is widely used for domestic service, supplied either in tanks or by pipelines. It is also used to augment natural-gas deliveries on peak days and by some industries as a standby fuel.

Other Gaseous Fuels

Hydrogen Hydrogen is used extensively in the production of ammonia and chemicals, in the hydrogenation of fats and oils, and as an oven reducing atmosphere. It is also used as a fuel in industrial cutting and welding operations. There are no resources of uncombined hydrogen as there are of the other fuels. It is made industrially by the steam reforming of natural gas, as the by-product of industrial operations such as the thermal cracking of hydrocarbons and the production of chlorine, and, to a lesser extent, by the electrolysis of water, which is a practically inexhaustible source.

Hydrogen is seen as the ultimate nonpolluting form of energy; when electrochemically combined with oxygen in fuel cells, only water, heat, and electricity are produced. Means for transforming the world's fossil energy economy into a hydrogen economy are being considered as a long-term option. Hydrogen can be stored in gaseous, liquid, or solid forms; however, currently available technologies are not suited to meet mass energy market needs. Technologies for economically producing, storing, and utilizing hydrogen are being researched in the United States, Europe, and Japan.

Acetylene Acetylene is used primarily in operations requiring high flame temperature, such as welding and metal cutting. To transport acetylene, it is dissolved in acetone under pressure and drawn into small containers filled with porous material.

Miscellaneous Fuels A variety of gases have very minor market shares. These include reformed gas, oil gases, producer gas, blue water gas, carbureted water gas, coal gas, and blast-furnace gas. The heating values of these gases range from 3.4 to 41 MJ/m^3 (90 to 1100 Btu/ft^3). They are produced by pyrolysis, the water gas reaction, or as by-products of pig-iron production.

Hydrogen sulfide in manufactured gases may range from approximately 2.30 g/m^3 (100 gr/100 ft^3) in blue and carbureted water gas to several hundred grains in coal- and coke-oven gases. Another important sulfur impurity is carbon disulfide, which may be present in amounts varying from 0.007 to 0.07 percent by volume. Smaller amounts of carbon oxysulfide, mercaptans, and thiophene may be found. However, most of the impurities are removed during the purification process and either do not exist in the finished product or are present in only trace amounts.

FUEL AND ENERGY COSTS

Fuel costs vary widely from one area to another because of the cost of the fuel itself and the cost of transportation. Any meaningful cost comparison between fuels requires current costs based on such factors as the amounts used at a particular geographical location, utilization efficiencies or energy-ratio data for the equipment involved, and the effects of "form value." Although the costs given in Table 27-9 do not apply to specific locations, they give fuel-cost trends.

TABLE 27-9 Time-Price Relationships for Fossil Fuels

Year	Bituminous coal and lignite, $/Mg ($/US ton)	Natural gas at the wellhead, $/1000 m^3 ($/1000 std ft^3)	Crude oil, domestic first purchase price, $/m^3 ($/bbl)
1975	21.15 (19.23)	15.55 (0.44)	48.23 (7.67)
1980	26.97 (24.52)	56.18 (1.59)	135.79 (21.59)
1985	27.61 (25.10)	88.69 (2.51)	151.51 (24.09)
1990	23.88 (21.71)	60.42 (1.71)	125.91 (20.03)
1993	21.77 (19.79)	71.73 (2.03)	89.62 (14.25)

SOURCE: *Annual Energy Review 1994*, Energy Information Administration, July 1995. Prices are national averages in current-year U.S. dollars for the year cited.

COAL CONVERSION

Coal is the most abundant fossil fuel, and it will be available long after petroleum and natural gas are scarce. However, because liquids and gases are more desirable fuel forms, technologies to convert coal into synthetic liquid and gaseous fuels have been developed. Current research, development, and demonstration efforts are aimed toward technical and economic improvements in some of the old, or first-generation, technologies and toward seeking new ways to accomplish the same ends: inexpensive and "clean" coal-conversion processes. However, as long as the price of petroleum remains near current levels, coal gasification and liquefaction technologies will remain uneconomic.

South Africa has the only commercial plant producing liquid transportation fuels and other products from coal. This technology will be described later.

Bodle, Vyas, and Talwalker (*Clean Fuels from Coal Symposium II*, Institute of Gas Technology, Chicago, 1975) presented the chart in Fig. 27-5, which shows very simply the different routes from coal to clean gases and liquids.

Coal Gasification

GENERAL REFERENCES: *Fuel Gasification Symp.*, 152d American Chemical Society Mtg., Sept. 1966. *Chemistry of Coal Utilization*, suppl. vol., Lowry (ed.), Wiley, New York, 1963; and 2d suppl. vol., Elliot (ed.), 1981. *Coal Gasification Guidebook: Status, Applications, and Technologies*, Electric Power Research Institute, EPRI TR-102034, Palo Alto, Calif., 1993. Notestein, *Commercial Gasifier for IGCC Applications Study Report*, U.S. Dept. of Energy, DOE/METC-91/6118, Morgantown Energy Technology Center, Morgantown, W. Va., 1990.

Background Converting coal to combustible gas has been practiced commercially since the early nineteenth century. The first gas-producing companies were chartered in 1812 in England and in 1816 in the United States to produce gas for illumination by the heating or pyrolysis of coal. This method of producing gas is still in use: the gas is a by-product of the carbonization of coal to manufacture coke for metallurgical purposes.

The advantages of a gaseous fuel as a source of heat and power increased the demand for gas and led to the invention of other methods of coal gasification. In the gas producer, introduced in the second half of the century, a downward-moving bed of coal or coke is reacted at atmospheric pressure with air and steam to create a fuel gas with a low heat value, in the range 3.4 to 6.0 MJ/m^3 (90 to 160 Btu/ft^3). Producer gas, as the product was named, soon enjoyed extensive industrial use, especially in steel manufacture. Gas producers, largely displaced by twentieth-century technology, are still employed in steel mills. A small version enhanced with modern handling and other technical improvements, the Wellman-Galusha producer, enjoys substantial use in small industry.

Driven by the same impetus, the development of the cyclic water-gas process in 1873 permitted the continuous production of gas of higher thermal content, about 13.0 MJ/m^3 (350 Btu/ft^3). Adding oil to the reactor increased the thermal content of the gas to 20.5 MJ/m^3 (550 But/ft^3). This type of fuel gas, carbureted water gas, was distributed in urban areas of the United States for residential and commercial uses until its displacement by lower-cost natural gas began in the 1940s. At approximately that time, development of oxygen-based gasification processes was initiated in the United States and in other countries. An early gasification process developed by Lurgi Kohle u Mineralöltechnik GmbH, which operated at elevated pressure, is still in use. Compositions of the coal gases produced by these methods,

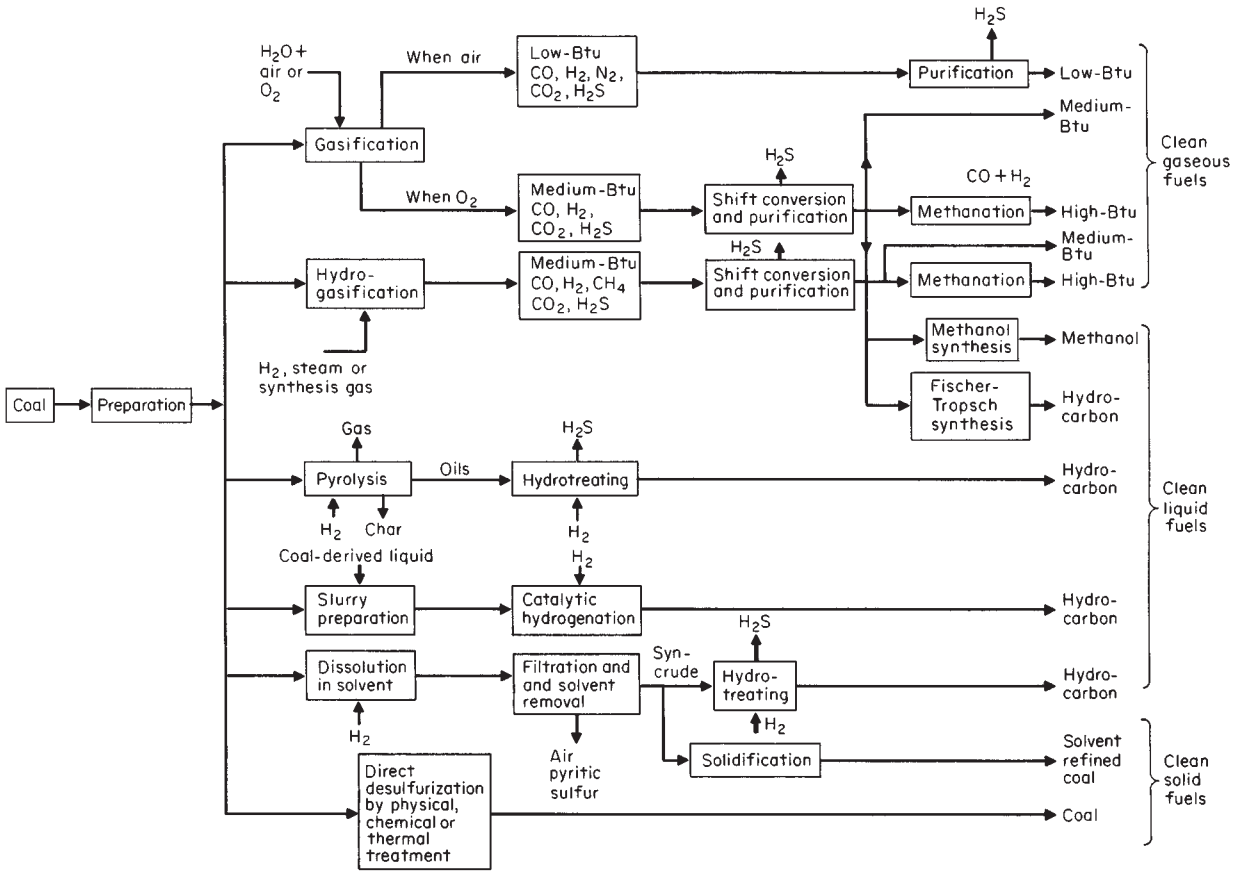


FIG. 27-5 The production of clean fuels from coal. (*Based on W. Bodle, K. Vyas, and A. Talwalker,* Clean Fuels from Coal Symposium II, *Institute of Gas Technology, Chicago, 1975.*)

which are referred to as the first-generation gasifiers, are listed in Table 27-10. There are a number of later-generation gasification technologies, as will be described in an ensuing subsection. The compositions of the gases produced by some of them are listed in Table 27-11.

Theoretical Considerations The chemistry of coal gasification can be depicted by conveniently assuming coal as carbon and by listing the several well-known reactions involved; see Table 27-12. Reaction (27-14) is the combustion of carbon and oxygen, which is highly exothermic. This reaction supplies most of the thermal energy for the gasification process. The oxygen may be pure or contained in air. Reactions (27-16) and (27-17) are endothermic and represent the conversion of carbon to combustible gases. These are driven by the heat energy supplied by reaction (27-14).

Hydrogen and carbon monoxide are produced by the gasification reaction, and they react with each other and with carbon. The reaction of hydrogen with carbon as shown in reaction (27-15) is exothermic and can contribute heat energy. Similarly, the methanation reaction (27-19) can contribute heat energy to the gasification. These equations are interrelated by the water-gas-shift reaction (27-18), the equilibrium of which controls the extent of reactions (27-16) and (27-17).

Several authors have shown (cf. Gumz, *Gas Producers and Blast Furnaces,* Wiley, New York, 1950; and Elliott and von Fredersdorff,

TABLE 27-10 Properties of Coal-Derived Gases

	Coke-oven gas	Producer gas	Water gas	Carbureted water gas	Synthetic coal gas
Reactant system	Pyrolysis	Air + steam	Steam (cyclic-air)	Steam + oil (cyclic-air)	Oxygen plus steam at pressure
Analysis, volume %*					
Carbon monoxide, CO	6.8	27.0	42.8	33.4	15.8
Hydrogen, H_2	47.3	14.0	49.9	34.6	40.6
Methane, CH_4	33.9	3.0	0.5	10.4	10.9
Carbon dioxide, CO_2	2.2	4.5	3.0	3.9	31.3
Nitrogen, N_2	6.0	50.9	3.3	7.9	
Other†	3.8	0.5	0.5	9.8	2.4
Fuel value, MJ/m^3	22.0	5.6	11.5	20.0	10.8
Btu/ft^3	(590)	(150)	(308)	(536)	290
Uses	Fuel, chemicals	Fuel	Fuel, chemicals	Fuel	Fuel, chemicals

*Analyses and fuel values vary with the type of coal and operating conditions.
†Other contents include hydrocarbon gases other than methane, hydrogen sulfide, and small amounts of other impurities.

TABLE 27-11 Coal-Derived Gas Compositions

Developer	Lurgi*	Texaco†[a]	BG/L†[b]	KRW*	KRW*	Shell†[c]
Type of bed	Moving	Entrained	Moving	Fluid	Fluid	Entrained
Coal feed form	Dry coal	Coal slurry	Dry coal	Dry coal	Dry coal	Dry coal
Coal type	Illinois #6	Illinois #6	Illinois #6	Illinois #6	Illinois #6	Illinois #5
Oxidant	Oxygen	Oxygen	Oxygen	Air	Oxygen	Oxygen
Pressure, MPa (psia)	0.101 (14.7)	4.22 (612)	2.82 (409)	2.82 (409)	2.82 (409)	2.46 (357)
Ash form	Slag	Slag	Slag	Agglomerate	Agglomerate	Slag
Composition, vol %						
H_2	52.2	30.3	26.4	15.7	27.7	26.7
CO	29.5	39.6	45.8	24.9	54.6	63.1
CO_2	5.6	10.8	2.9	5.3	4.7	1.5
CH_4	4.4	0.1	3.8	0.8	5.8	0.03
Other hydrocarbons	0.3	—	0.2	<0.01	<0.01	—
H_2S	0.9	1.0	1.0	—	1.3	1.3
COS	0.04	0.02	0.1	—	0.1	0.1
$N_2 + Ar$	1.5	1.6	3.3	47.0	1.7	5.2
H_2O	5.1	16.5	16.3	6.2	4.4	2.0
$NH_3 + HCN$	0.5	0.1	0.2	0.02	0.08	0.02
HCl	—	0.02	0.03	—	—	0.03
H_2S:COS	20:1	42:1	11:1	8:1	9:1	9:1

*Rath, "Status of Gasification Demonstration Plants," *Proc. 2d Annu. Fuel Cells Contract Review Mtg.,* DOE/METC-9090/6112, p. 91.
†*Coal Gasification Guidebook: Status, Applications, and Technologies,* Electric Power Research Institute, EPRI TR-102034, 1993. (*a*) page 5-28; (*b*) page 5-58; (*c*) page 5-48.

Chemistry of Coal Utilization, 2d suppl. vol., Lowry [ed.], Wiley, New York, 1963) that there are three fundamental reactions: the Boudouard reaction (27-17), the heterogeneous water-gas reaction (27-18), and the hydrogasification reaction (27-15). The equilibrium constants for these reactions are sufficient to calculate all the reactions listed.

It is not possible, however, to calculate accurately actual gas composition by using the relationships of reactions (27-14) to (27-19) in Table 27-12. Since the gasification of coal always takes place at elevated temperatures, thermal decomposition (pyrolysis) takes place as coal enters the gasification reactor. Reaction (27-15) treats coal as a compound of carbon and hydrogen and postulates its thermal disintegration to produce carbon (coke) and methane. Reaction (27-21) assumes the stoichiometry of hydrogasifying part of the carbon to produce methane and carbon.

It is possible to utilize these reactions and their relationships with each other for predicting the effects of changes in the operating parameters of gasification. At higher temperatures, endothermic reactions are favored at the expense of exothermic reactions. Methane production will decrease as reactions (27-15) and (27-19) proceed at a lower rate, CO production will be favored, and all reaction rates will increase in the direction in which heat absorption takes place. An increase in pressure will favor those reactions in which the number of moles of products is less than the number of moles of reactants. At higher pressures, production of CO_2 will be favored as well as that of methane. The knowledge of stoichiometry, equilibrium conditions, and rates for these gasification reactions provides a sound basis for modeling and extrapolating gasification systems.

A great deal depends on the gasifier system, coal reactivity and particle size, and method of contacting coal with gaseous reactants (steam and air or oxygen). It is generally believed that oxygen reacts completely in a very short distance from the point at which it is mixed or comes in contact with coal or char. The heat evolved acts to pyrolyze the coal, and the char formed then reacts with carbon dioxide, steam, or other gases formed by combustion and pyrolysis. The assumption made in Table 27-12 that the solid reactant is carbon is probably close to being correct. The conversion of coal to char and the type of char formed affect the kinetics of gas-solid reactions. While the reaction rate does vary with temperature, as in all chemical reactions, the overall rate of reaction is controlled probably by the chemical reaction rate below 1273 K (1832°F). Above this, pore diffusion has an overriding effect, and at very high temperatures surface-film diffusion probably controls. Thus, for many gasification processes the reactivity of the char is quite important. This may depend not only on parent-coal characteristics but also on the method of heating, rate of heating, and particle-gas dynamics.

The importance of these concepts can be illustrated by the extent to which the pyrolysis reactions contribute to gas production. In a moving-bed gasifier (e.g., producer-gas gasifier), the particle is heated through several distinct thermal zones. At the initial heat-up zone, coal carbonization or devolatilization dominates. In the successively hotter zones, char devolatilization, char gasification, and fixed carbon

TABLE 27-12 Chemical Reactions in Coal Gasification

Reaction	Reaction heat, kJ/(kg·mol)	Process	Number
	Solid-gas reactions		
$C + O_2 \rightarrow CO_2$	+393,790	Combustion	(27-14)
$C + 2H_2 \rightarrow CH_4$	+74,900	Hydrogasification	(27-15)
$C + H_2O \rightarrow CO + H_2$	−175,440	Steam-carbon	(27-16)
$C + CO_2 \rightarrow 2CO$	−172,580	Boudouard	(27-17)
	Gas-phase reaction		
$CO + H_2O \rightarrow H_2 + CO_2$	+2,853	Water-gas shift	(27-18)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	+250,340	Methanation	(27-19)
	Pyrolysis and hydropyrolysis		
CH_x	$\left(1-\frac{X}{4}\right)C + \left(\frac{X}{4}\right)CH_4$	Pyrolysis	(27-20)
$CH_x + m\ H_2$	$\left[1-\left(\frac{X+2m}{4}\right)\right]C + \left(\frac{X+2m}{4}\right)CH_4$	Hydropyrolysis	(27-21)

combustion are the dominant processes. About 17 percent of total gas production occurs during the coal devolatilization phase, and about 23 percent is produced during char devolatilization. The balance, typically about 60 percent of the total, is produced during the char gasification and combustion phases. This emphasizes the importance of coal quality or reactivity.

Gasifier Types and Characteristics The fundamental chemistry and physics of gasification motivate the design of existing and advanced gasifiers. The equations listed in Table 27-12 show that an appropriate means of contacting a solid particle with a gaseous reactant is expedient, that the transfer of heat within the gasifier (and to the gasifier) is a critical parameter, and that variations in pressure and temperature alter the composition of the gas produced. In addition, the type of coal and the composition of both organic and inorganic constituents have a strong influence on gas composition and applicability of various gasification systems.

The three main types of reactors shown in Fig. 27-6 are in actual commercial use: the moving bed, the fluidized bed, and the entrained bed. The moving bed is often referred to as a *fixed* bed because the coal bed is kept at a constant height. These differ in size, coal feed, reactant and product flows, residence time, and reaction temperature.

Gasification-Based Power Systems Today's single most important driving force for the coal gasification market development is gasification-based power generation, named the *integrated gasification combined-cycle* (IGCC) power system (Fig. 27-7). The coal is crushed prior to gasification and partially burned, through the addition of steam and air or oxygen, to produce the high-temperature (1033 to 2255 K [1400 to 3600°F], depending on the type of gasifier) reducing environment necessary for gasification. The fuel gas passes through a heat recovery and cleanup section where particulate (dust) and sulfur are removed. After cleanup, the fuel gas, composed primarily of hydrogen and carbon oxides, is burned with compressed air and expanded through a gas turbine to generate electricity. Heat is recovered from the turbine's hot exhaust gas to produce steam (at subcritical conditions), which is expanded in a steam turbine for additional electricity generation.

The three basic types of gasifiers already mentioned have been incorporated into IGCC plant designs. Within each gasifier type, the oxidant can be air or oxygen, and the coal feed can be dry or in slurry form. Furthermore, the gas cleanup (i.e., particulate and sulfur removal) can be performed at high temperature (i.e., hot-gas cleanup) or lower temperature (cold-gas cleanup). The constituents of the fuel gas, as well as the pressure and temperature conditions at the gasifier exit, are determined by the type of gasifier employed. The efficiency and economics of an IGCC power system are highly dependent on the various parameters described above.

There are three unique features of the power system depicted in Fig. 27-7. These features assure that the IGCC-based power system is

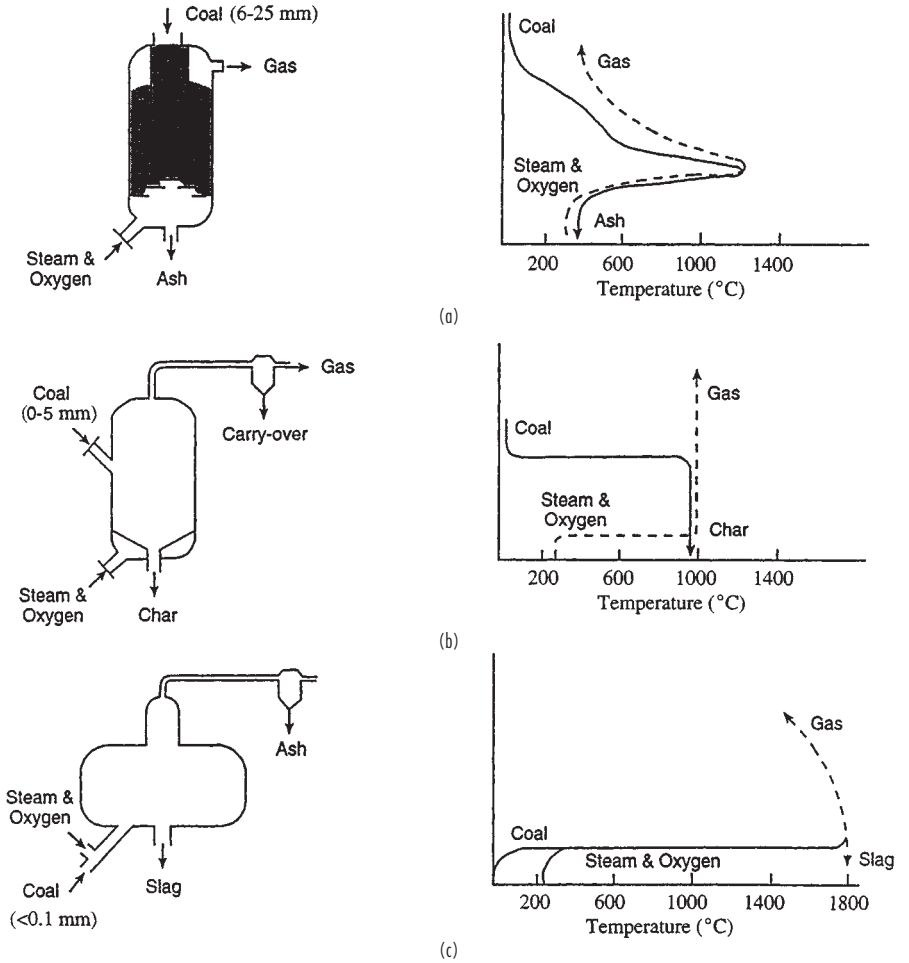


FIG. 27-6 Gasifier types and temperature profiles: (*a*) fixed bed (nonslagging); (*b*) fluidized bed; (*c*) entrained flow. (°C = K – 273)

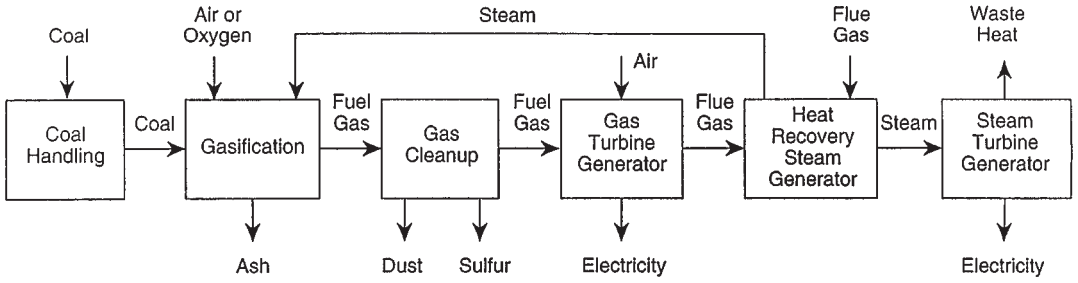


FIG. 27-7 Integrated gasification combined-cycle block diagram.

lower in cost and more thermally efficient than a conventional pulverized-coal combustion system and that it is environmentally superior to it. First, the gas mass flow rate from a gasifier is about one fourth that from a combustor because the former is oxygen-blown and operates substoichiometrically, and the combustor is air-blown and operates with excess air. Because of the elevated operating pressure, the volumetric gas flow to the hydrogen sulfide conversion unit is actually 60 times less than the volumetric flow to the flue gas desulfurization unit, and this lowers the capital cost of the gas cleanup system. Second, the sulfur in coal-derived fuel gas is present as hydrogen sulfide, which can more readily be separated from the fuel gas than sulfur dioxide can be separated from flue gas. Additionally, hydrogen sulfide can be easily converted to elemental sulfur, a more valuable by-product than the calcium sulfate produced when lime is used to remove sulfur dioxide from combustion flue gas. Third, the IGCC system generates electricity by both gas and steam turbines—corresponding to Brayton (gas) and Rankine (steam) cycles—compared to the conventional power plant's steam-only generating system.

Current Status The U.S. Department of Energy (DOE) and its private-sector collaborators have substantially advanced the development of gasification-based power systems during the last decade. This section describes the current status for the various types of gasifiers used.

Moving Bed Depending on the temperature at the base of the coal bed, the ash can either be dry or in the form of molten slag. If excess steam is added, the temperature can be kept below the ash fusion point. In that case the coal bed rests on a rotating grate which allows the dry ash to fall through for removal. To reduce the steam usage, a slagging bottom gasifier has been developed in Scotland by British Gas and Lurgi (BG/L) in which the ash is allowed to melt and drain off through a slag tap. This gasifier has over twice the capacity per unit area of the dry-bottom gasifier. The gas composition from a BG/L gasifier is listed in Table 27-11.

The capacity of the demonstration gasifier in Scotland depends on coal quality; the gasifier can handle a coal input of 750 GJ/h, equivalent to more than 25,000 kg/h (55,115 lb/h) of coal or 70,000 m^3/h (2,500,000 ft^3/h) of gas production. The Clean Energy Demonstration Project, cost-shared by the DOE under the Clean Coal Technology Program, will test the scale-up of the BG/L oxygen-blown, slagging gasifier from demonstration to commercial size. Multiple BG/L units will provide coal gas for a 477-MW IGCC plant to be located on an eastern U.S. site.

Fluidized Bed The possibility of coal and ash agglomeration is eliminated by a fluidized-bed gasifier developed by Westinghouse and M. W. Kellogg. Char and ash that exit the gasifier with the product gas are recycled to the hot agglomerating and jetting zone where temperatures are high enough to pyrolyze fresh coal that is introduced there, gasify the char, and soften the ash particles. The ash particles stick together and fall to the base of the gasifier, where they are cooled and removed. Agglomerating gasifiers achieve better carbon conversion than conventional fluidized-bed gasifiers. The compositions of two gas streams based on air-blown and oxygen-blown gasifiers are listed in Table 27-11.

The agglomerating fluid-bed gasifier can be blown by either air or oxygen at 2.8 MPa (406 psia) pressure. Pressurized operation has several advantages: slightly higher methane formation, resulting in higher heating value of the gas; increased heat from the methanation reactions, which reduces the amount of oxygen needed; reduced heat losses through the wall and, consequently, improved efficiency; and higher generating capacity. Limestone can be added to remove a major portion of the sulfur contained in the coal.

The advanced pressurized fluid-bed gasifiers currently ready for demonstration have internal diameters of around 3.6 m (12 ft) and are 20 to 28 m (66 to 92 ft) in height. Production of more than 100,000 m^3/h of gas (at gasifier temperature and pressure) is achieved by the advanced gasifiers, equivalent to 33,260 kg/h of bituminous coal (air blown).

The KRW (Kellogg-Rust-Westinghouse) gasification process uses an agglomerating-ash fluidized-bed gasifier in which crushed limestone can be injected with the coal for sulfur capture. The Piñon Pine 100-MW IGCC plant built near Reno, Nevada, uses the KRW gasifier. This IGCC plant, scheduled to begin commercial operation in 1997, is being built with U.S. DOE sponsorship under the Clean Coal Technology Program.

Another fluidized-bed gasification technology is the Tampella U-Gas gasifier. This technology was developed by the Institute of Gas Technology (IGT) in Chicago and licensed by the Finnish boiler manufacturer, Tampella. Like the KRW gasifier, it is an air-blown, agglomerating-ash gasifier that uses limestone for in-bed sulfur capture. The two primary differences between the KRW and Tampella gasifiers are the way the gas velocity and temperature in the agglomerating zone are controlled and how the ash and spent limestone discharge is controlled.

Entrained Bed The two primary examples of oxygen-blown, dry-feed, entrained-flow gasifiers are Shell and PRENFLO. These two gasifiers share common roots and are very similar. The gas composition from a Shell gasifier is listed in Table 27-11. An advantage of Shell coal gasification technology is the lack of feed coal limitations. A wide variety of coals (from anthracite to brown coal) have been successfully tested. As with other entrained-flow gasifiers, disadvantages of the Shell process include a high oxygen requirement and a high waste heat recovery duty. However, the ability to feed dry coal reduces the oxygen requirement below that of single-stage entrained-flow gasifiers that use slurry feed and makes the Shell gasifier somewhat more efficient. The penalty for this small efficiency improvement is a more complex coal-feeding system. Like the Shell, the PRENFLO gasification process uses pressurized, dry-feed, entrained-flow technology with water-cooled gasifier vessels. The primary difference between the two processes is in the design of the syngas cooler. While the Shell process uses cooled recycle gas to partially cool the hot syngas before heat recovery, the PRENFLO process uses a radiant water-wall boiler with fins (to increase the surface area for heat transfer) that is connected directly to the gasifier. The PRENFLO gasifier was selected for a 300-MW IGCC project in Puertollano, Spain, to begin operation in 1996. The project is funded by power companies from several European countries and by the European Community.

Cost of Gasification-Based Power Systems In the U.S. power industry the capital cost is usually reported in dollars per kilowatt ($/kW) and the cost of electricity (COE) in mills per kilowatt-hour (a mill is one thousandth of a dollar). Estimation of capital cost and COE

is more complex than it seems. The power industry is a regulated industry that uses a different approach than one used by a typical chemical process industry. This approach, an accepted standard procedure in the power industry, is well documented in the *Technical Assessment Guide* (Electric Power Research Institute, EPRI TR-102276-V1 R7, Palo Alto, Calif., 1993). As part of the standard procedure, the assignment of the capital formation structure (i.e., the percentages of bonds, common stock, preferred stock), inflation rate, escalation rate, and assumptions in process and project contingencies are not necessarily the same as those used in the process industry. Process industry practitioners are urged to consult the *Technical Assessment Guide* for more in-depth understanding of capital cost and cost of electricity, as well as meaningful comparisons of different power systems. Comparison of power systems is further complicated by the many different parameters assumed in the cost determination. Cost of coal; sulfur content, moisture content, and other properties of coal; ambient temperature; level of integration between various component units; model of gas turbine; gas cleanup method; year of estimation—all these and other factors may have significant impacts on cost.

While comparison of the absolute capital costs and costs of electricity among different power systems is difficult and uncertain, the structure of these costs is rather typical, and the costs of component units are usually within known ranges. For an oxygen-blown IGCC power system, the breakdown of the capital cost for the four component units is: air separation plant (11 to 17 percent), fuel gas plant (33 to 42 percent), combined-cycle unit (32 to 39 percent), and balance of plant (2 to 21 percent). The breakdown of the cost of electricity is: capital charge (52 to 56 percent), operating and maintenance (14 to 17 percent), and fuel (28 to 32 percent).

The capital investment required for gasification-based power systems is 1400 to 1600 $/kW (1994 US dollars) and is projected to become less than 1200 $/kW in the year 2000 because of the higher efficiency associated with gas-turbine combined-cycles currently being designed by turbine vendors.

Development is under way for a gasification-based power system using a cascaded humidified advanced turbine. The power system is the same as the IGCC system in the front end (i.e., the gasification section without heat recovery and the gas-cleanup section) but differs from IGCC in the back end (i.e., the power generation section). Instead of combined steam and gas cycles as used in the IGCC system, the humidified turbine system uses only the gas turbine, eliminating the steam cycle. Because of this simplification and the corresponding elimination of the expensive coal-gas cooler, the power system based on the advanced humidified turbine offers further reduction in the capital investment requirement. Depending upon how the advanced turbine system is configured with the front end section, the capital investment requirement is expected to be on the order of 1000 $/kW.

Direct Coal Liquefaction

General References: *Chemistry of Coal Utilization*, suppl. vol., Lowry (ed.), Wiley, New York, 1963, and 2d suppl. vol., Elliott (ed.), 1981. Wu and Storch, *Hydrogenation of Coal and Tar*, U.S. Bur. Mines Bull. 633, 1968. Srivastava, McIlvried, Gray, Tomlinson, and Klunder, *American Chemical Society Fuel Chemistry Division Preprints*, Chicago, 1995.

Background The primary objective of any coal-liquefaction process is to increase the hydrogen-to-carbon ratio and remove sulfur, nitrogen, oxygen, and ash. Table 27-13 shows the hydrogen-to-carbon ratios in proceeding from coal to crude petroleum to gasoline, together with the four techniques for accomplishing coal liquefaction. Direct coal liquefaction refers to any process in which coal and hydrogen are directly reacted at high pressure and temperature. A hydrogen donor solvent and/or catalyst may also be present. The first two techniques in Table 27-13 (direct hydrogenation and solvent extraction) follow this approach. A pyrolysis process is included in Table 27-13 for comparison. The fourth technique, catalytic hydrogenation of carbon monoxide, or indirect liquefaction (discussed later in this subsection), first converts coal to synthesis gas, which is purified and reacted over a catalyst to form liquid products. One version of the indirect-liquefaction route converts purified synthesis gas to methanol, for direct fuel use or for conversion to gasoline.

TABLE 27-13 Basic Approaches of Coal Conversion to Liquid Hydrocarbons

1. Direct hydrogenation at elevated temperature and pressure, with or without catalysts
2. Solvent extraction (hydrogen donor)
3. Pyrolysis
4. Catalytic hydrogenation of carbon monoxide

	Bituminous coal	Lignite	Crude petroleum	Gasoline
H/C	0.8	0.7	1.8	1.9

The technology for coal liquefaction to synthetic fuels is not new. In 1913 Dr. Friedrich Bergius discovered the technique of adding hydrogen to coal at a pressure of 20.3 MPa (2940 psia) and a temperature of about 723 K (842°F). Under these conditions most oxygen was hydrogenated to water, some nitrogen to ammonia, and most sulfur to hydrogen sulfide. Hydrogen was also chemically combined with the coal to produce a liquid similar to petroleum. Production of synthetic liquid fuels and chemicals from coal in Germany increased in the mid-1920s, and by 1939 gasoline was being produced by coal hydrogenation in Germany at 910 Gg/a (1×10^6 US ton/a) and in England at 136 Gg/a (150,000 US ton/a). In the early 1950s, the U.S. Bureau of Mines constructed and operated a demonstration plant at Louisiana, Missouri, using the technology of catalytic hydrogenation of coal to produce liquid fuels.

The oil price shocks of the 1970s accelerated the U.S. development of direct coal liquefaction processes to the pilot plant stage (up to 227 Mg/d [250 US ton/d] coal feed rate) of several competing designs, such as the solvent-refined coal (SRC), Exxon donor solvent (EDS), and H-Coal processes. These are discussed briefly in a following subsection. Both the SRC and H-Coal process designs include equipment for generating products ranging from heavy boiler fuels to higher-grade transportation fuels.

In the United States, it became clear after the return of low oil prices in the 1980s that the existing processes would not be able to compete economically, and research proceeded on a smaller scale to improve the efficiency of coal liquefaction for the production of high-value distillate fuels. Key aspects of the process improvement are more effective hydrogen utilization through catalysis and better solids rejection technology. A two-stage concept has been developed that tailors reaction conditions in the first stage to coal solubilization with some cracking, and in the second stage to production of additional liquids with product upgrading. Both supported Ni/Mo catalysts and slurry catalysts are being tested to maximize yields of distillate products that are completely compatible with the existing refinery infrastructure.

A nearer-term variant of direct coal liquefaction is the coprocessing of mixtures of coal and heavy petroleum residua. The coal solids are thought to preferentially "getter" the nickel and vanadium contaminants, typically present in low-value residua, that rapidly poison supported catalysts during conventional resid upgrading. The petroleum component acts as a slurry vehicle for pumping the coal into the reactors, thereby avoiding process recycle requirements. A further advantage is the lowered hydrogen uptake per unit of product. The coprocessing concept can be extended to mixtures of coal and municipal waste such as mixed plastics. Landfill disposal costs are avoided, while, at the same time, carbon values from the waste contribute to the transportation fuel supply.

Direct-Liquefaction Kinetics All direct-liquefaction processes consist of three basic steps: (1) coal slurrying in a vehicle solvent, (2) coal dissolution under high pressure and temperature, and (3) transfer of hydrogen to the dissolved coal. However, the specific reaction pathways and associated kinetics are not known in detail. Overall reaction schemes and semiempirical relationships have been generated by the individual process developers, but applications are process specific and limited to the range of the specific data bases. More extensive research into liquefaction kinetics has been conducted on the laboratory scale, and these results are discussed below.

Depending on its rank, coal can be dissolved in as little as one minute in the temperature range of 623 to 723 K (662 to 842°F) in suitable solvents, which are assumed to promote thermal cracking of the coal into smaller, more readily dissolved fragments. These fragments may be stabilized through reactions with one another or with hydrogen supplied either by a donor solvent or from a gas phase.

Data on Illinois No. 6 and Kentucky No. 9 coals were used by Wen and Han (*Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **20**(1): 216–233, 1975) to obtain a rate equation for coal dissolution under hydrogen pressure. These data included a temperature range of 648 to 773 K (705 to 930°F) and pressures up to 13.8 MPa (2000 psia). An empirical rate expression was proposed as

$$r_A = k_0 \left[\exp\left(\frac{-E}{RT}\right) \cdot \exp\left(0.0992\, P_{H_2}\right) \right] (C_{so})\,(1-x)\left(\frac{C}{S}\right) \qquad (27\text{-}22)$$

where r_A = rate of dissolution, g/(h·cm^3 reactor volume)
C_{so} = weight fraction of organics in original coal
k_0 = rate constant, g/(h·cm^3) reactor volume
P_{H_2} = hydrogen partial pressure, MPa
x = conversion, solid organics/solid organics in original coal
C/S = coal-solvent weight ratio
E = energy of activation, kcal/(g·mol)
R = universal gas constant, 1.987×10^{-3} kcal/(g mol·K)
T = temperature, K.

Calculated and measured conversions agreed when the Arrhenius temperature dependency indicated in Eq. (27-22) was used with the following values for the parameters:

Constant	Illinois No. 6	Kentucky No. 9
k_0, g/(h·cm^3)	2125	15.3
E, kcal/g·mol)	11	4.5

The low activation energies suggested that the dissolution rate is controlled by counterdiffusion of organic components from the coal surface and dissolved hydrogen from the solvent. Also, the rate of dissolution appeared to depend exponentially on hydrogen partial pressure.

A free-radical mechanism has been proposed for coal dissolution in hydrogen donor solvents. Solvents and high temperatures facilitate degradation of coal to form relatively low-molecular-weight free radicals, which may be stabilized by hydrogen transfer from a hydroaromatic solvent. Initial dissolution is considered to be a thermal process, with a net rate dependent upon the type of solvent and its effectiveness in stabilizing free radicals. The greater a solvent's hydrogen donor capability, the more effective it is in terminating radicals. In continuous recycle process configurations, the overall rate-limiting step appears to be rehydrogenation of the donor solvent, which is a function of the dissolved hydrogen and catalyst. Nitrogen and sulfur removal and the formation of light liquid products are considered to result primarily from catalytic effects.

The conversion reaction from coal to oil has been modeled as a series of steps:

$$\text{Coal} + \text{solvent} \rightarrow \text{preasphaltene} \rightarrow \text{asphaltene} \rightarrow \text{oil}$$

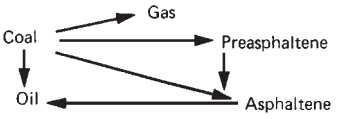
with some gas formation accompanying each step. In a study using Illinois No. 6 coal and 505 to 727 K (450 to 850°F) boiling-range process-derived heavy distillate, data were obtained at 13.8 MPa (2000 psia) and 673 to 748 K (750 to 885°F). Activation energies for the steps of the reaction series were determined to be:

Reaction step	Activation energy, kcal/g·mol
Preasphaltene → asphaltene	15
Asphaltene → oil	21
Coal → preasphaltene	32

At 723K (843°F), stoichiometries for the reaction steps were represented as:

$$\text{Coal} + 3\ \text{solvent} \rightarrow \text{preasphaltene}$$
$$\text{Preasphaltene} \rightarrow 2\ \text{asphaltene}$$
$$\text{Asphaltene} \rightarrow 3\ \text{oil}$$

A more complex reaction model was proposed from the results of a kinetic study of thermal liquefaction of subbituminous coal. Data were obtained over a temperature range of 673 to 743 K (752 to 878°F) at 13.8 MPa (2000 psia) by using two solvents, hydrogenated anthracene oil (HAO), and hydrogenated phenanthrene oil (HPO), at a coal-solvent ratio of 1:15. Results were correlated with the following model:



Activation energies and frequency factors for the various steps of this model were determined as follows:

Reaction	Rate constant	Activation energy, kcal/(g·mol)		Frequency factor, min^{-1}	
		Coal-HAO	Coal-HPO	Coal-HAO	Coal-HPO
Coal → oil	k_o	14.1	28.9	3.11×10^3	2.1×10^8
Coal → preasphaltene	k_p	13.8	4.3	2.81×10^3	4.94
Coal → asphaltene	k_a	15.6	8.6	1.12×10^4	9.63×10^1
Coal → gas	k_g	21.5	10.5	8.72×10^5	3.85×10^2
Preasphaltene → asphaltene	k_{pa}	12.8	33.9	9.66×10^2	2.48×10^9
Asphaltene → oil	k_{ao}	16.0	25.6	1.42×10^3	1.53×10^7

Magnitudes of k_g, k_p, k_a, and k_o indicate the importance of direct reactions with coal, where k_{pa} and k_{ao} are for hydrocracking reactions in the conversion process. Data for k_o and k_{ao} from the experiments with HPO indicate that oil production from coal is increased by the use of a good hydrogen donor solvent.

Direct-Liquefaction Processes Figure 27-8 presents a simplified process flow diagram of a typical direct coal liquefaction plant. Specific processes are described in the following paragraphs.

Solvent-Refined Coal (SRC) This processing concept was initiated by the Pittsburgh & Midway Coal Mining Co. in the early 1960s. The *SRC-I process* operating mode is designed to produce a solid fuel for utility applications. Typical operating conditions and product yields for SRC-I are shown in Table 27-14.

The *SRC-II process* is an improved version of the SRC process that recycles a portion of the reactor effluent slurry in place of the distillate solvent of the SRC-I process. The primary product is a liquid distillate fuel with a 490 to 728 K (423 to 851°F) boiling range. This is achieved in part by increased severity of operating conditions, but also by establishing a higher concentration of resid reactant and catalytic mineral matter in the reactor through slurry recycle. The net reactor effluent slurry is passed to a vacuum-flash unit for separation of the distillate product from the mineral matter and undissolved coal, thereby avoiding the filtration step. Typical operating conditions and product yields for SRC-II are shown in Table 27-14.

Exxon Donor Solvent (EDS) Process The EDS process, developed by the Exxon Research and Engineering Co., liquefies coal by use of a hydrogen donor solvent under hydrogen pressure in an upflow, plug-flow reactor. The solvent is a catalytically hydrogenated recycle stream, fractionated from the middle boiling range, 474 to 728 K (395 to 850°F), of the liquid product. Hydrogenation of the recycle solvent is conducted in a conventional fixed-bed catalytic reactor using hydrotreating catalysts, such as cobalt molybdate or nickel molybdate. Coal conversion and liquid yield strongly depend on the molecular composition, boiling-point range, and other properties of the solvent. Exxon uses its proprietary Solvent Quality Index (SQI) as the main criterion of solvent quality and correlates product yields with SQI. Typical operating conditions and product yields are shown in Table 27-14.

Vacuum distillation is used to remove the residue from the distillate product. Additional heavy oil may be recovered from the vacuum bottoms by employing Exxon's Flexicoking process.

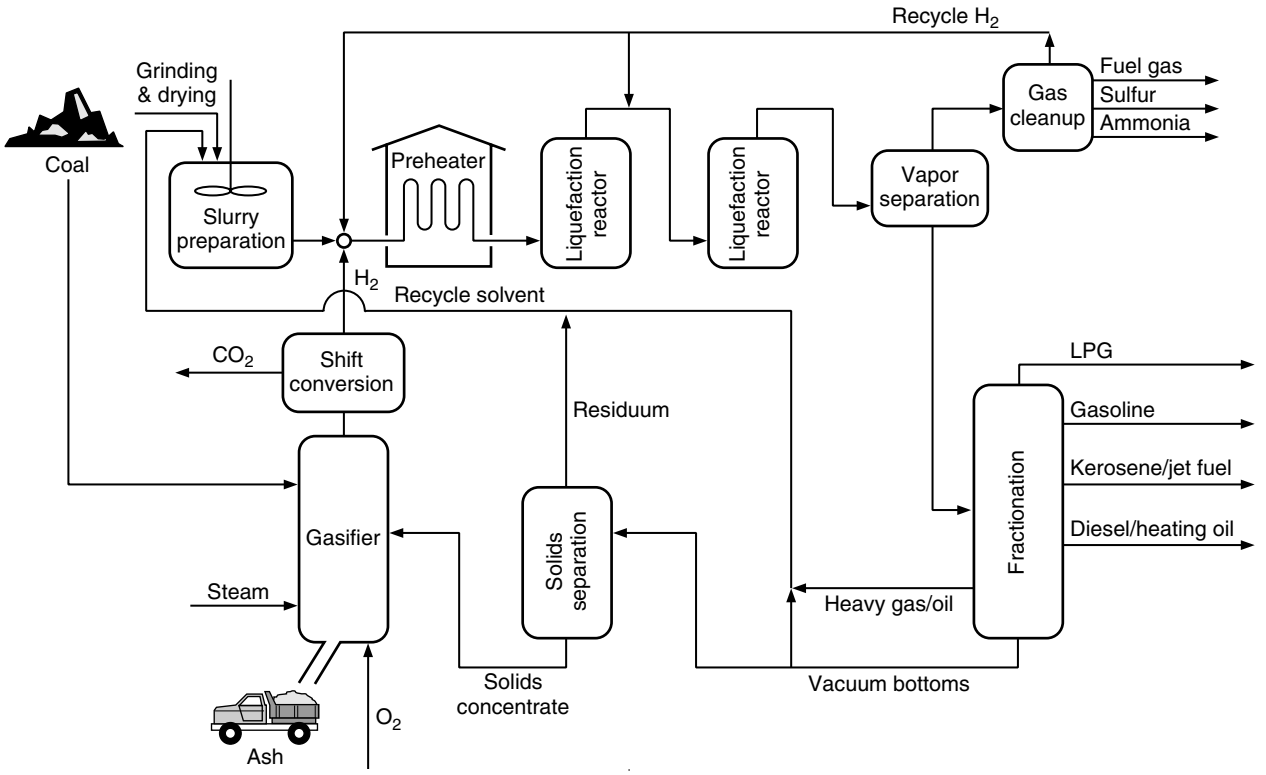


FIG. 27-8 Direct liquefaction of coal.

H-Coal Process The H-Coal process, based on H-Oil technology, was developed by Hydrocarbon Research, Inc. (HRI). Depending on the type of products desired, the process can be operated in either a fuel-oil mode or a syncrude mode by adjusting operating severity. The heart of the process is a three-phase fluidized reactor (ebullated-bed) in which catalyst pellets are fluidized by the upward flow of slurry and gas through the reactor. Catalyst activity in the reactor is maintained by the withdrawal of small quantities of spent catalyst and the addition of fresh catalyst. The reactor contains an internal tube for recirculating the reaction mixture through the catalyst bed.

Solids separation is accomplished by vacuum distillation in the syncrude mode. Table 27-14 shows the product yields obtained in PDU tests with an Illinois No. 6 bituminous coal.

Two-Stage Liquefaction This is an advanced process that provides improved, lower-cost technology by the more efficient and specific application of catalysis in the reaction stages. Higher yields of better-quality products are obtained by recovering and recycling heavy intermediates to extinction. Unconverted coal and mineral matter are removed by conventional technology such as supercritical solvent extraction or vacuum distillation. Several variations of this approach have been tested at the Advanced Coal Liquefaction R&D Facility (5.4 Mg/d or 6 US ton/d scale) in Wilsonville, Alabama. Distillate yields as high as 78 percent (moisture and ash-free basis) have been achieved. Wilsonville operating and product data are shown in Table 27-14. An economic evaluation is given in a later section.

Further development of staged-liquefaction technology options is being conducted by Hydrocarbon Technologies, Inc. (HTI, formerly HRI) in their 2.7-Mg/d (3-US ton/d) proof-of-concept unit (Lawrenceville, New Jersey), and more advanced concepts are being researched by HTI and others at the bench scale. Recent HTI results are presented in Table 27-14. Coal-derived product quality has been improved dramatically (less than 50 ppm nitrogen content, for example) through use of in-line fixed-bed hydrotreating of the product stream. Slurry catalysts are being employed in addition to the more conventional supported catalysts as a means of simplifying reactor designs and removing process constraints.

Coal-Oil Coprocessing In this approach, coal is slurried in petroleum resid rather than recycle solvent, and both coal and petroleum components are converted to high-quality fuels in the reaction stages. This variation offers the potential for significant cost reduction by eliminating or reducing internal recycle oil streams. More important, fresh hydrogen requirements are reduced because the petroleum resid feedstock component has a higher initial hydrogen content. As a result, plant capital investment is reduced substantially. It also offers the opportunity for accelerating the introduction of coal-derived liquid fuels into the marketplace by utilizing, to a much greater degree, existing petroleum refining facilities and technology.

Other carbonaceous materials such as municipal waste plastics, cellulosics, and used motor oils may also serve as cofeedstocks with coal in this technology.

Coal Pyrolysis Coal pyrolysis produces synthetic crude oil, gas, and char. In the COED process, crushed coal is dried and heated to successively higher temperatures in a series of fluidized-bed reactors. In each stage, a portion of the coal's volatile matter is released. Typically, four stages at 589, 727, 811, and 1089 K (600, 850, 1000, and 1500°F), respectively, are used, but operations vary owing to the need to stay below the coal agglomeration temperature. Process heat is generated by burning char in the last stage and circulating hot char and gases to the other stages. Volatile products are condensed in a recovery system and the pyrolysis oil is filtered to remove fines.

Typical pyrolysis yields and oil qualities for two bituminous coals, Utah A and Illinois No. 6, are presented in Table 27-15. The major problem with any pyrolysis process is the high yield of char.

Flash Pyrolysis Coal is rapidly heated to elevated temperatures for a brief period of time to produce oil, gas, and char. The increase in hydrogen content in the gases and liquids is the result of removing carbon from the process as a char containing a significantly reduced amount of hydrogen. Several processes have been tested on a rela-

TABLE 27-14 Direct Liquefaction Process Conditions and Product Yields

Developer	Gulf[a]	Gulf	Exxon	HRI	SCS,[b] EPRI, Amoco	HTI
Process	SRC-I	SRC-II	EDS	H-Coal	Two-stage	Two-stage
Coal type	Kentucky 9 & 14	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6
Operating conditions						
Nominal reactor residence time, h	0.5	0.97	0.67			
Coal space velocity per stage, kg/(h·m³) (lb/[h·ft³])				530 (33.1)	825[c] (51.7)	310 (19.4)
1st stage						
Temperature, K (°F)	724 (842)	730 (855)	722 (840)	726 (847)	695 (791)	680 (765)
Total pressure, MPa (psia)	10.3 (1500)	13.4 (1950)	10.3 (1500)			19.2 (2790)
H_2 partial pressure, MPa (psia)	9.7 (1410)	12.6 (1830)		12.6 (1827)	18.3 (2660)	
Catalyst type	Coal minerals	Coal minerals	Coal minerals	Supported catalyst (Co/Mo)	AKZO-AO-60 (Ni/Mo)	AKZO-AO-60 (Ni/Mo)
Catalyst replacement rate, kg/kg (lb/US ton) mf coal					7.5×10^{-4} (1.5)	8×10^{-4} (1.6)
2d Stage						
Temperature, K (°F)					705 (809)	705 (810)
Total pressure, MPa (psia)						18.6 (2700)
H_2 partial pressure, MPa (psia)					17.0 (2470)	
Catalyst type					AKZO-AO-60 (Ni/Mo)	AKZO-AO-60 (Ni/Mo)
Catalyst replacement rate kg/kg (lb/US ton) mf coal					7.5×10^{-4} (1.5)	1.5×10^{-3} (3.0)
Product yields, wt % maf coal						
H_2	–2.4	–4.7	–4.3	–5.9	–6.0	–7.2
H_2O	—	—	12.2[d]	8.3	9.7	9.8
H_2S, CO_x, NH_3	—	—	4.2[e]	5.0	5.2	5.2
C_1-C_3	3.7[f]	15.8[f]	7.3	11.3	6.5	5.6
C_4^+ distillate	13.5[g]	47.3[g]	38.8	53.1	65.6	73.3
Bottoms[h]	68.4	28.0	41.8	28.2	19.0	13.3
Unreacted coal[i]	5.4	5.0	—	6.4	7.0	5.0
Distillate end point, K (°F)	727 (850)	727 (850)	911 (1180)	797 (975)	797 (975)	524 (975)

[a] In partnership with Pittsburg & Midway Coal Mining Co.
[b] Southern Company Services, Inc., prime contractor for Wilsonville Facility.
[c] Coal space velocity is based on settled catalyst volume.
[d] CO_x is included.
[e] CO_x is excluded.
[f] C_4 is included.
[g] C_4 is excluded.
[h] Unreacted coal is included.
[i] "Unreacted coal" is actually insoluble organic matter remaining after reaction.

TABLE 27-15 Pyrolysis Data

	Illinois No. 6 seam	Utah A seam
Net yields, wt % dry coal		
Char	59.5	54.5
Oil	19.3	21.5
Gas	15.1	18.3
Liquor	6.1	5.7
Net process yields		
Char, kg/kg (lb/US ton)	0.595 (1190)	0.545 (1090)
Oil, m³/kg (bbl/US ton)	1.92×10^{-4} (1.10)	2.15×10^{-4} (1.23)
Gas, m³/kg (std ft³/US ton)	0.274 (8810)	0.266 (8545)
Liquor, dm³/kg (gal/US ton)	0.061 (14.6)	0.057 (13.7)
Oil properties		
Elemental Analysis, wt %, dry		
Carbon	79.6	83.8
Hydrogen	7.1	9.5
Nitrogen	1.1	0.9
Sulfur	2.8	0.4
Oxygen	8.5	5.0
Ash	0.9	0.3
Relative density, 288 K (°API, 60°F)	1.110 (–4)	1.105 (–3.5)
Moisture, wt %	0.8	0.5
Pour point, K (°F)	311 (100)	311 (100)
Kinematic viscosity, mm²/s, 372 K (SUS 210°F)	300 (1333)	87.5 (390)
Solids, wt %, dry basis	4.0	3.8
Higher heating value, MJ/kg (Btu/lb)	35.0 (15,050)	37.4 (16,100)

tively small scale. None have demonstrated economic potential, although the technical concepts appear to be valid.

Indirect Coal Liquefaction

General References: Dry, *The Fischer-Tropsch Synthesis, Catalysis Science and Technology,* vol. 1, Springer-Verlag, New York, 1981. Anderson, *The Fischer-Tropsch Synthesis,* Academic Press, New York, 1984. Sheldon, *Chemicals from Synthesis Gas,* D. Reidel Publishing Co., Dordrecht, Netherlands, 1983. Rao, Stiegel, Cinquegrane, and Srivastava, "Iron-based Catalyst for Slurry-phase Fischer-Tropsch Process: Technology Review," *Fuel Processing Technology* **30:** 83–151, 1992.

Background Indirect coal liquefaction differs fundamentally from direct coal liquefaction in that the coal is first converted to a synthesis gas (a mixture of H_2 and CO) which is then converted over a catalyst to the final product. Figure 27-9 presents a simplified process flow diagram for a typical indirect coal liquefaction process. The synthesis gas is produced in a gasifier (see a description of coal gasifiers earlier in this section), where the coal is partially combusted at high temperature and moderate pressure with a mixture of oxygen and steam. In addition to H_2 and CO, the raw synthesis gas contains other constituents (such as CO_2, H_2S, NH_3, N_2, and CH_4), as well as particulates.

Before being fed to the synthesis reactor, the synthesis gas must first be cooled and then passed through particulate removal equipment. Following this, depending on the catalyst being used, it may be necessary to adjust the H_2/CO ratio. Modern high-efficiency gasifiers typically produce a ratio between 0.45 and 0.7, which is lower than stoichiometric for the synthesis reaction. Some catalysts, particularly iron catalysts, possess water gas shift conversion activity and permit

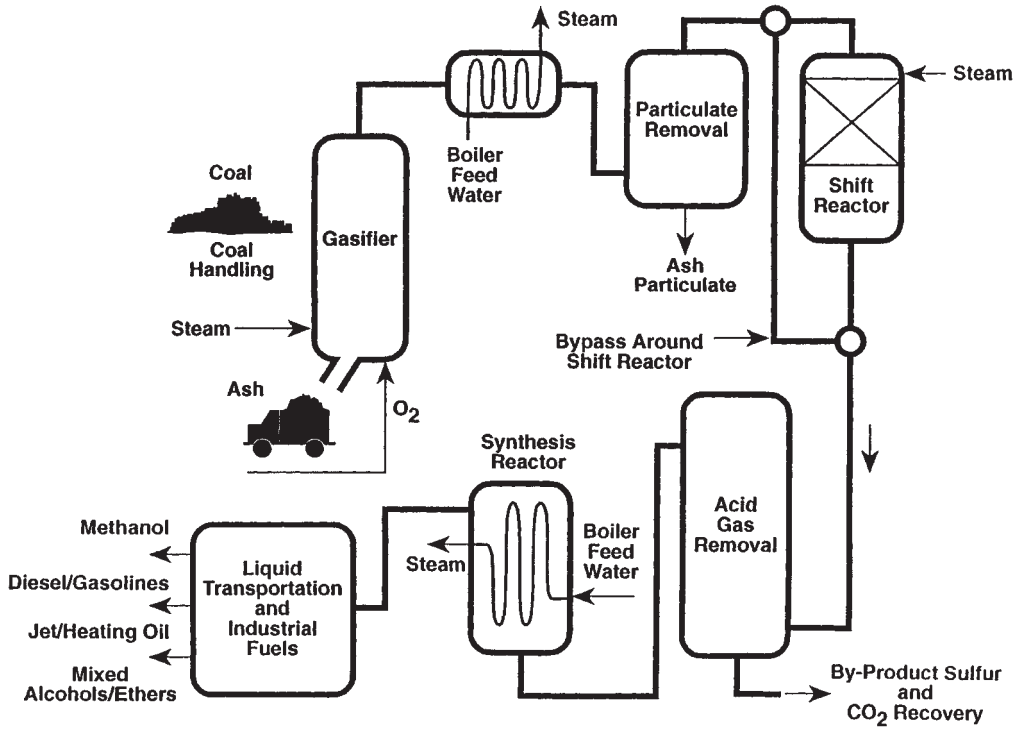


FIG. 27-9 Indirect liquefaction of coal.

operation with a low H_2/CO ratio. Other catalysts possess little shift activity, however, and require a ratio adjustment before the synthesis reactor.

After shift conversion, acid gases (CO_2 and H_2S) are scrubbed from the synthesis gas. A guard chamber is sometimes used to remove the last traces of H_2S. The cleaned gas is sent to the synthesis reactor, where it is converted at moderate temperature and pressure, typically 498 to 613 K (435 to 645°F) and 1.52 to 6.08 MPa (220 to 880 psia). Products from the process depend on operating conditions and the catalyst employed, as well as reactor design. Typical products include hydrocarbons (mainly straight chain paraffins from methane through n-C_{50} and higher), oxygenates (methanol, higher alcohols, ethers), and other chemicals (olefins).

Fischer-Tropsch Synthesis The best-known technology for producing hydrocarbons from synthesis gas is the Fischer-Tropsch synthesis. This technology was first demonstrated in Germany in 1902 by Sabatier and Senderens when they hydrogenated carbon monoxide (CO) to methane, using a nickel catalyst. In 1926 Fischer and Tropsch were awarded a patent for the discovery of a catalytic technique to convert synthesis gas to liquid hydrocarbons similar to petroleum.

The basic reactions in the Fischer-Tropsch synthesis are:

Paraffins:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad (27\text{-}23)$$

Olefins:

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \qquad (27\text{-}24)$$

Alcohols:

$$2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad (27\text{-}25)$$

Other reactions may also occur during the Fischer-Tropsch synthesis, depending on the catalyst employed and the conditions used:

Water-gas shift:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (27\text{-}26)$$

Boudouard disproportionation:

$$2CO \rightarrow C(s) + CO_2 \qquad (27\text{-}27)$$

Surface carbonaceous deposition:

$$\left(\frac{2x+y}{2}\right) H_2 + xCO \rightarrow C_xH_y + xH_2O \qquad (27\text{-}28)$$

Catalyst oxidation-reduction:

$$yH_2O + xM \rightarrow M_xO_y + yH_2 \qquad (27\text{-}29)$$

$$yCO_2 + xM \rightarrow M_xO_y + yCO \qquad (27\text{-}30)$$

Bulk carbide formation:

$$yC + xM \rightarrow M_xC_y \qquad (27\text{-}31)$$

where M represents a catalytic metal atom.

The production of hydrocarbons using traditional Fischer-Tropsch catalysts is governed by chain growth or polymerization kinetics. The equation describing the production of hydrocarbons, commonly referred to as the Anderson-Schulz-Flory equation, is:

$$\log\left(\frac{W_n}{n}\right) = n \log \alpha + \log\left[\frac{(1-\alpha)^2}{\alpha}\right] \qquad (27\text{-}32)$$

where W_n = weight fraction of products with carbon number n, and α = chain growth probability, i.e., the probability that a carbon chain on the catalyst surface will grow by adding another carbon atom rather than terminating. In general, α is dependent on temperature, pressure, and catalyst composition but independent of chain length. As α increases, the average carbon number of the product also increases. When α equals 0, only methane is formed. As α approaches 1, the product becomes predominantly wax.

Figure 27-10 provides a graphical representation of Eq. (27-32) showing the weight fraction of various products as a function of the chain growth parameter α. This figure shows that there is a particular α that will maximize the yield of a desired product, such as gasoline or

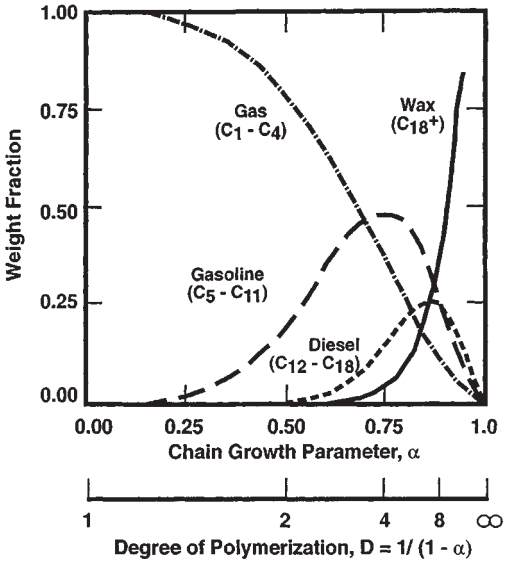


FIG. 27-10 Product yield in Fischer-Tropsch synthesis.

diesel fuel. The weight fraction of material between carbon numbers m and n, inclusive, is given by:

$$W_{mn} = m\alpha^{m-1} - (m-1)\alpha^{m} - (n+1)\alpha^{n} + n\alpha^{n+1} \qquad (27\text{-}33)$$

The α to maximize the yield of the carbon number range from m to n is given by:

$$\alpha_{opt} = \left(\frac{m^2 - m}{n^2 + n}\right)^{\frac{1}{n-m+1}} \qquad (27\text{-}34)$$

Additional gasoline and diesel fuel can be produced through further refining, such as hydrocracking or catalytic cracking of the wax product.

The Fischer-Tropsch reaction is highly exothermic. Therefore, adequate heat removal is critical. High temperatures result in high yields of methane, as well as coking and sintering of the catalyst. Three types of reactors (tubular fixed bed, fluidized bed, and slurry) provide good temperature control, and all three types are being used for synthesis gas conversion. The first plants used tubular or plate-type fixed-bed reactors. Later, SASOL, in South Africa, used fluidized-bed reactors, and most recently, slurry reactors have come into use.

Fischer-Tropsch synthesis reactor operation can be classified into one of two categories: high-temperature, 613 K (645°F), or low-temperature, 494 to 544 K (430 to 520°F), operation. The Synthol reactor developed by SASOL is typical of high-temperature operation. Using an iron-based catalyst, this process produces a very good gasoline product having high olefinicity and a low boiling range. The olefin fraction can readily be oligomerized to produce diesel fuel. Low-temperature operation, typically in fixed-bed reactors, produces a much more paraffinic and straight-chain product. Selectivity can be tailored to give the desired chain growth parameter. The primary diesel fraction, as well as the diesel-range product from hydrocracking of the wax, is an excellent diesel fuel.

Oxygenates and Chemicals A whole host of oxygenated products, i.e., fuels, fuel additives, and chemicals, can be produced from synthesis gas. These include such products as methanol, ethylene, isobutanol, dimethyl ether, dimethyl carbonate, and many other hydrocarbons and oxyhydrocarbons. Typical oxygenate-producing reactions are:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (27\text{-}35)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (27\text{-}36)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (27\text{-}37)$$

Reaction (27-37) can occur in parallel with the methanol reactions, thereby overcoming the equilibrium limitation on methanol formation. Higher alcohols can also be formed, as illustrated by Reaction (27-25), which is applicable to the formation of either linear or branched alcohols.

The production of methyl acetate from synthesis gas is currently being practiced commercially. Following methanol synthesis, as shown by Reaction (27-35), the reactions are:

$$CH_3OH + CO \rightarrow CH_3COOH \qquad (27\text{-}38)$$

$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O \qquad (27\text{-}39)$$

Acrylates and methacrylates, which are critical to the production of polyesters, plastics, latexes, and synthetic lubricants, can also be produced from these oxygenated intermediates.

Status of Indirect Liquefaction Technology The only commercial indirect coal liquefaction plants for the production of transportation fuels are operated by SASOL in South Africa. Construction of the original plant was begun in 1950, and operations began in 1955. This plant employs both fixed-bed (Arge) and entrained-bed (Synthol) reactors. Two additional plants were later constructed with start-ups in 1980 and 1983. These latter plants employ dry-ash Lurgi Mark IV coal gasifiers and entrained-bed (Synthol) reactors for synthesis gas conversion. These plants currently produce 45 percent of South Africa's transportation fuel requirements, and, in addition, they produce more than 120 other products from coal.

SASOL has pursued the development of alternative reactors to overcome specific operational difficulties encountered with the fixed-bed and entrained-bed reactors. After several years of attempts to overcome the high catalyst circulation rates and consequent abrasion in the Synthol reactors, a bubbling fluidized-bed reactor 1 m (3.3 ft) in diameter was constructed in 1983. Following successful testing, SASOL designed and constructed a full-scale commercial reactor 5 m (16.4 ft) in diameter. The reactor was successfully commissioned in 1989 and remains in operation.

SASOL and others, including Exxon, Statoil, Air Products and Chemicals, Inc., and the U.S. Department of Energy, have engaged in the development of slurry bubble column reactors for Fischer-Tropsch and oxygenate synthesis. SASOL, in fact, commissioned a slurry reactor with a 5-m diameter in 1993. It doubled the wax capacity of the SASOL I facility. The development work on this kind of reactor shows that it has several advantages over competing reactor designs: (1) excellent heat transfer capability resulting in isothermal reactor operations, (2) high catalyst and reactor productivity, (3) ease of catalyst addition and withdrawal, (4) simple construction, and (5) ability to process hydrogen-lean synthesis gas successfully. Because of the small particle size of the catalyst used in the slurry reactor, however, effective separation of catalyst from the products is difficult but is crucial to successful operation.

The United States has two commercial facilities that convert coal to fuels and chemicals by indirect liquefaction. The Great Plains Synfuels Plant, located in Beulah, North Dakota, produces synthetic natural gas (SNG) from North Dakota lignite by Lurgi dry-ash gasification technology and methanation. Operated by Dakota Gasification Company (DGC), the plant converts approximately 15.4 Gg (17,000 US tons) of lignite per day to about 4.7×10^6 Nm^3 (166×10^6 std ft^3) of pipeline-quality gas in 14 Lurgi gasifiers. Aromatic naphtha and tar oil are also produced in the gasification section. The plant operates at 120 percent of its original design capacity. In addition to SNG, there is a wide assortment of other products, e.g., anhydrous ammonia, sulfur, phenol, cresylic acid, naphthas, and krypton/xenon.

Eastman Chemical Company has operated a coal-to-methanol plant in Kingsport, Tennessee, since 1983. Two Texaco gasifiers (one is a backup) process 34 Mg/h (37 US ton/h) of coal to synthesis gas. The synthesis gas is converted to methanol by use of ICI methanol technology. Methanol is an intermediate for producing methyl acetate and acetic acid. The plant produces about 225 Gg/a (250,000 US ton/a) of acetic anhydride. As part of the DOE Clean Coal Technology Program, Air Products and Chemicals, Inc., and Eastman Chemical Company are constructing a 9.8-Mg/h (260-US ton/d) slurry-phase reactor for the conversion of synthesis gas to methanol and dimethyl

ether. Construction is expected to be completed in November 1996. Despite the success of SASOL, most of the commercial interest in Fischer-Tropsch synthesis technology is based on natural gas, and it is likely to remain so as long as the gas is abundant and inexpensive. In 1985, Mobil commercialized its Methanol-to-Gasoline (MTG) technology in New Zealand, natural gas being the feedstock. This fixed-bed process converts synthesis gas to 4 Gg (4400 US tons) of methanol per day; the methanol can then be converted to 2290 m^3/d (14,400 bbl/d) gasoline. Owing to economic factors, the plant is used primarily for the production of methanol.

Shell Gas B.V. has constructed a 1987 m^3/d (12,500 bbl/d) Fischer-Tropsch plant in Malaysia, start-up occurring in 1994. The Shell Middle Distillate Synthesis (SMDS) process, as it is called, uses natural gas as the feedstock to fixed-bed reactors containing cobalt-based catalyst. The heavy hydrocarbons from the Fischer-Tropsch reactors are converted to distillate fuels by hydrocracking and hydroisomerization. The quality of the products is very high, the diesel fuel having a cetane number in excess of 75.

Exxon Research and Engineering Company has developed a process for converting natural gas to high-quality refinery feedstock, the AGC-21 Advanced Gas Conversion Process. The technology involves three highly integrated process steps: fluid-bed synthesis gas generation; slurry-phase Fischer-Tropsch synthesis; and mild fixed-bed hydroisomerization. The process was demonstrated in the early 1990s with a slurry-phase reactor having a diameter of 1.2 m (4 ft) and a capacity of about 32 m^3/d (200 bbl/d).

The largest Fischer-Tropsch facility based on natural gas is the Mossgas plant located in Mossel Bay, South Africa. Natural gas is converted to synthesis gas in a two-stage reformer and subsequently converted to hydrocarbons by SASOL's Synthol technology. The plant, commissioned in 1992, has a capacity of 7155 m^3/d (45,000 bbl/d).

TABLE 27-16 Estimated Costs of Direct Coal Liquefaction Plant (1993 US dollars)

Elements of cost	Baseline costs* $ million	Improved design due to R&D effort†
Coal handling	222	226
Liquefaction	942	823
Gas cleanup/by-product recovery	297	297
Product hydrotreating	107	113
De-ashing unit	46	43
Gasification	334	302
Air separation	244	220
Inside boundary limits field costs	2192	2024
Outside boundary limits field costs	978	968
Total field cost	3170	2992
Total capital	3889	3670
Refined product costs,‡ $/m^3$		
Capital§	148.49	129.12
Coal	49.31	47.23
Catalyst	16.16	1.45
Natural gas	22.58	16.92
Labor	10.44	9.50
Other O&M	2.08	1.89
By-product credits	(26.29)	(20.44)
Required Selling Price	227.77	183.77
Quality premium	(7.48)	(7.48)
Crude oil equivalent price ($/bbl)¶	215.28 (34.22)	176.29 (28.02)
Plant output, Mm^3/a (M bbl/a)	3.85 (24.2)	4.23 (26.6)

*Costs based on plant processing 26,105 Mg/d (28,776 US ton/d) of Illinois No. 6 coal. Source: *Direct Coal Liquefaction Baseline Design and Systems Analysis,* prepared by Bechtel and Amoco under DOE contract no. DE-AC22-90PC89857, March 1993.

†Source: Klunder and McIlvried, unpublished DOE Pittsburgh Energy Technology Center data.

‡To obtain $/bbl from $/$m^3$, multiply by 0.1590.

§Includes maintenance materials, taxes, and insurance.

¶The difference between the required selling price and the crude oil equivalent price represents the enhanced value of the coal liquids, due to their all-distillate and low-heteroatom character.

Economics of Coal Liquefaction Bechtel developed conceptual commercial designs (greenfield), based on 1993 costs and representing current state-of-the-art technologies, for both direct and indirect coal liquefaction facilities feeding Illinois and Wyoming coals. The direct liquefaction design focuses on producing hydrotreated distillate products. The conceptual baseline plant is designed to process about 26.3 Gg/d (29,000 US ton/d) of coal while producing about 11,130 m^3/d (70,000 bbl/d) of distillate products. The design employs Texaco gasifiers for hydrogen production, supercritical solvent de-ashing for removing unconverted coal and mineral matter from the products, and high-pressure ebullated-bed reactors for coal hydrogenation. Table 27-16 presents the capital and operating costs. As shown, the crude oil equivalent price for direct liquefaction products is approximately \$215/m^3 (\$34/bbl). Additional cases were evaluated to assess the impact on product costs of technological advances through continued R&D. The final column in Table 27-16 shows the impact of such advances as improvements in product yields, space velocity, catalyst recovery, and hydrogen production on the cost of production. A required selling price of \$176/m^3 (\$28/bbl) (1993 US dollars) is believed to be achievable following further R&D.

The indirect liquefaction baseline design is for a plant of similar size. Unlike the direct liquefaction baseline, the design focuses on producing refined transportation fuels by use of Shell gasification technology. Table 27-17 shows that the crude oil equivalent price is approximately \$216/m^3 (\$34/bbl). Additional technological advances in the production of synthesis gas, the Fischer-Tropsch synthesis, and product refining have the potential to reduce the cost to \$171/m^3 (\$27/bbl) (1993 US dollars), as shown in the second column of Table 27-17.

Coproduction of electricity along with synthesis gas conversion offers the potential for significant cost savings. The once-through liquid-phase methanol technology was developed specifically for this

TABLE 27-17 Estimated Costs of Indirect Coal Liquefaction Plant (1993 US Dollars)

Elements of cost	Baseline costs,* $ million	Costs with R&D improvements	Once-through Fischer-Tropsch
Coal handling	207	207	207
Gasification	1018	1018	1018
Air separation	466	323	453
Gas cleaning/by-product recovery	195	195	192
Fischer-Tropsch synthesis	331	190	286
Synthesis gas recycle loop	403	352	79
Product refining	209	131	155
Inside battery limits field cost	2829	2416	2390
Power generation	119	254	419
Outside battery limits field cost	488	481	452
Total field cost	3436	3151	3261
Total plant cost	4283	3927	4063
Total capital	4620	4231	4346
Refined product costs,† $/$m^3$			
Capital‡	155.91	147.55	193.02
Coal	63.90	61.57	84.03
Catalyst	12.45	12.01	16.95
Other O&M	34.47	30.94	42.52
Power	7.80	−12.83	−118.74
Required selling price	274.53	229.25	217.17
Crude oil equivalent price ($/bbl)§	216.04 (34.34)	170.75 (27.14)	158.68 (25.23)
Plant output, Mm^3/a (Mbbl/a)	3.77 (23.7)	3.91 (24.6)	2.86 (18.0)
Power, MW			1176

SOURCE: *Proc. Coal Liquefaction and Gas Conversion Contractors Review Conf.,* CONF-9508133, Pittsburgh Energy Technology Center, Pittsburgh, Pa., 1995.

*Costs based on plant processing 26,105 Mg/d (28,776 US ton/d) of Illinois No. 6 coal.

†To obtain $/bbl from $/$m^3$, multiply by 0.1590.

‡Includes maintenance, materials, taxes, and insurance.

§The difference between the required selling price and the crude oil equivalent price represents the enhanced value of the coal liquids, due to their all-distillate and low-heteroatom character.

objective to be realized in *integrated gasification combined cycle* (IGCC) power plants. *Once-through Fischer-Tropsch* (OTFT) in conjunction with IGCC has a similar potential, as indicated by the final column in Table 27-17. This concept has the potential for reducing the cost of products from Fischer-Tropsch to a crude oil equivalent price of \$159/m^3 (\$25/bbl).

For the related gas-based technology, Shell and SASOL have separately estimated that their technologies, on large scale and with natural-gas feedstock, can compete with crude oil priced at \$126 to 145/m^3 (\$20 to 23/bbl). The cost of production for each plant is sensitive to plant location and the price of the natural-gas feedstock.

At the current stage of development, direct and indirect liquefaction technologies look equally attractive economically, and both have the potential for significant cost improvements.

HEAT GENERATION

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COMBUSTION BACKGROUND

Basic Principles

Theoretical Oxygen and Air for Combustion The amount of oxidant (oxygen or air) just sufficient to burn the carbon, hydrogen, and sulfur in a fuel to carbon dioxide, water vapor, and sulfur dioxide is the *theoretical* or *stoichiometric oxygen* or *air* requirement. The chemical equation for complete combustion of a fuel is

$$C_xH_yO_zS_w + \left(\frac{4x + y - 2z + 4w}{4}\right) O_2 = xCO_2 + \left(\frac{y}{2}\right) H_2O + wSO_2 \qquad (27\text{-}40)$$

x, y, z, and w being the number of atoms of carbon, hydrogen, oxygen, and sulfur, respectively, in the fuel. For example, 1 mol of methane (CH_4) requires 2 mol of oxygen for complete combustion to 1 mol of carbon dioxide and 2 mol of water. If air is the oxidant, each mol of oxygen is accompanied by 3.76 mol of nitrogen.

The volume of theoretical oxygen (at 0.101 MPa and 298 K) needed to burn any fuel can be calculated from the ultimate analysis of the fuel as follows:

$$24.45\left(\frac{C}{12} + \frac{H}{4} - \frac{O}{32} + \frac{S}{32}\right) = m^3O_2/\text{kg fuel} \qquad (27\text{-}41)$$

where C, H, O, and S are the decimal weights of these elements in 1 kg of fuel. (To convert to ft^3 per lb of fuel, multiply by 16.02.) The mass of oxygen (in kg) required can be obtained by multiplying the volume by 1.31. The volume of theoretical air can be obtained by using a coefficient of 116.4 in Eq. (27-41) in place of 24.45.

Figure 27-11 gives the theoretical air requirements for a variety of combustible materials on the basis of fuel higher heating value (HHV). If only the fuel lower heating value is known, the HHV can be calculated from Eq. (27-6). If the ultimate analysis is known, Eq. (27-7) can be used to determine HHV.

Excess Air for Combustion More than the theoretical amount of air is necessary in practice to achieve complete combustion. This excess air is expressed as a percentage of the theoretical air amount. The *equivalence ratio* is defined as the ratio of the actual fuel-air ratio to the stoichiometric fuel-air ratio. Equivalence ratio values less than 1.0 correspond to fuel-*lean* mixtures. Conversely, values greater than 1.0 correspond to fuel-*rich* mixtures.

Products of Combustion For lean mixtures, the *products of combustion* (POC) of a sulfur-free fuel consist of carbon dioxide, water vapor, nitrogen, oxygen, and possible small amounts of carbon monoxide and unburned hydrocarbon species. Figure 27-12 shows the effect of fuel-air ratio on the flue gas composition resulting from the combustion of natural gas. In the case of solid and liquid fuels, the POC may also include solid residues containing ash and unburned carbon particles.

Equilibrium combustion product compositions and properties may be readily calculated using thermochemical computer codes which minimize the Gibbs free energy and use thermodynamic databases

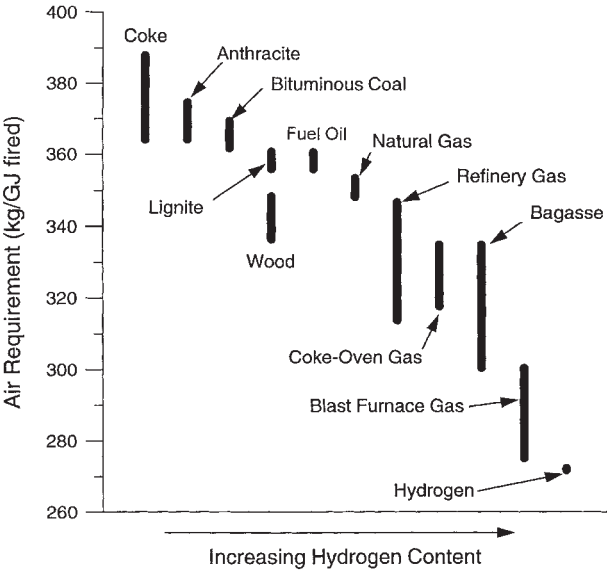


FIG. 27-11 Combustion air requirements for various fuels at zero excess air. To convert from kg air/GJ fired to lb air/10^6 Btu fired, multiply by 2.090.

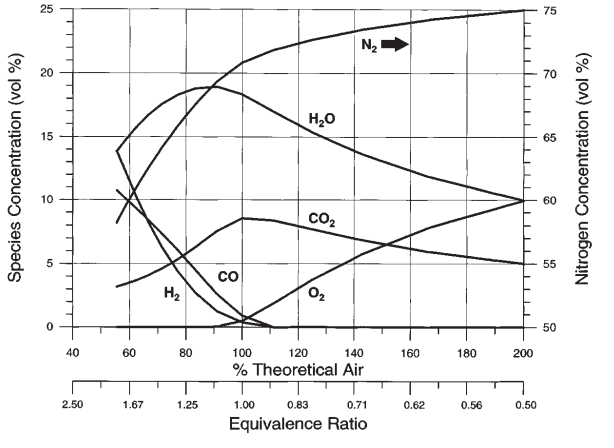


FIG. 27-12 Effect of fuel-air ratio on flue-gas composition for a typical U.S. natural gas containing 93.9% CH_4, 3.2% C_2H_6, 0.7% C_3H_8, 0.4% C_4H_{10}, 1.5% N_2 and 1.1% CO_2 by volume.

containing polynomial curve-fits of physical properties. Two widely used versions are those developed at NASA Lewis (Gordon and McBride, NASA SP-273, 1971) and at Stanford University (Reynolds, *STANJAN Chemical Equilibrium Solver,* Stanford University, 1987).

Flame Temperature The heat released by the chemical reaction of fuel and oxidant heats the POC. Heat is transferred from the POC, primarily by radiation and convection, to the surroundings, and the resulting temperature in the reaction zone is the flame temperature. If there is no heat transfer to the surroundings, the flame temperature equals the theoretical, or adiabatic, flame temperature.

Figure 27-13 shows the *available heat* in the products of combustion for various common fuels. The available heat is the total heat released during combustion minus the flue-gas heat loss (including the heat of vaporization of any water formed in the POC).

Flammability Limits There are both upper (or rich) and lower (or lean) limits of flammability of fuel-air or fuel-oxygen mixtures. Outside these limits, a self-sustaining flame cannot form. Flammability limits for common fuels are listed in Table 27-18.

Flame Speed Flame speed is defined as the velocity, relative to the unburned gas, at which an adiabatic flame propagates normal to itself through a homogeneous gas mixture. It is related to the combustion reaction rate and is important in determining burner flashback and blow-off limits. In a premixed burner, the flame can *flash back* through the flameholder and ignite the mixture upstream of the burner head if the mixture velocity at the flameholder is lower than the flame speed. Conversely, if the mixture velocity is significantly higher than the flame speed, the flame may not stay attached to the flameholder and is said to *blow off.* Flame speed is strongly dependent on fuel/air ratio, passing from nearly zero at the lean limit of flammability through a maximum and back to near zero at the rich limit of flammability. Maximum flame speeds for common fuels are provided in Table 27-18.

Pollutant Formation and Control in Flames Key combustion-generated air pollutants include nitrogen oxides (NO_x), sulfur oxides (principally SO_2), particulate matter, carbon monoxide, and unburned hydrocarbons.

Nitrogen Oxides Three reaction paths, each having unique characteristics (see Fig. 27-14), are responsible for the formation of NO_x during combustion processes: (1) *thermal* NO_x, which is formed by the combination of atmospheric nitrogen and oxygen at high temperatures; (2) *fuel* NO_x, which is formed from the oxidation of fuel-bound nitrogen; and (3) *prompt* NO_x, which is formed by the reaction of fuel-derived hydrocarbon fragments with atmospheric nitrogen. (NO_x is

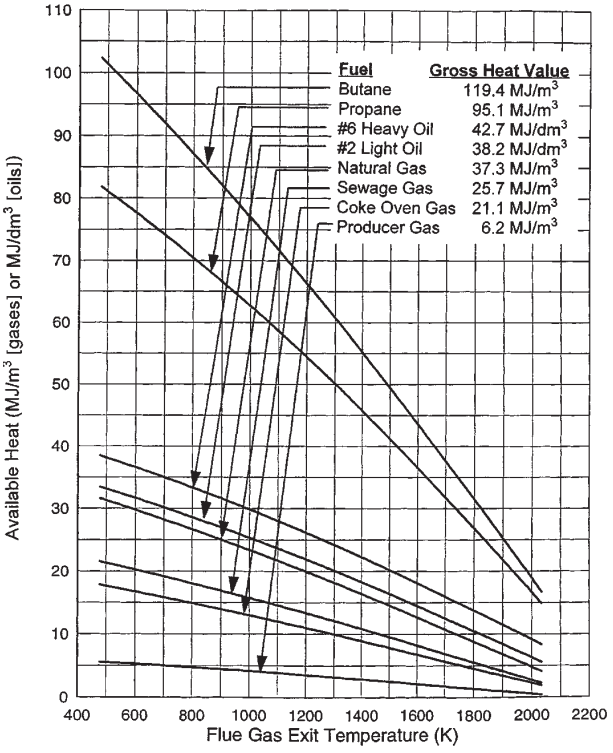


FIG. 27-13 Available heats for some typical fuels. The fuels are identified by their gross (or higher) heating values. All available heat figures are based upon complete combustion and fuel and air initial temperature of 288 K (60°F). To convert from MJ/Nm³ to Btu/ft³, multiply by 26.84. To convert from MJ/dm³ to Btu/gal, multiply by 3588.

TABLE 27-18 Combustion Characteristics of Various Fuels*

Fuel	Minimum ignition temp., K/°F	Calculated flame temperature,† K/°F		Flammability limits, % fuel gas by volume in air		Maximum flame velocity, m/s and ft/s		% theoretical air for max. flame velocity
		in air	in O_2	lower	upper	in air	in O_2	
Acetylene, C_2H_2	578/581	2905/4770	3383/5630	2.5	81.0	2.67/8.75	—	83
Blast furnace gas	—	1727/2650	—	35.0	73.5	—	—	—
Butane, commercial	753/896	2246/3583	—	1.86	8.41	0.87/2.85	—	—
Butane, *n*-C_4H_{10}	678/761	2246/3583	—	1.86	8.41	0.40/1.3	—	97
Carbon monoxide, CO	882/1128	2223/3542	—	12.5	74.2	0.52/1.7	—	55
Carbureted water gas	—	2311/3700	3061/5050	6.4	37.7	0.66/2.15	—	90
Coke oven gas	—	2261/3610	—	4.4	34.0	0.70/2.30	—	90
Ethane, C_2H_4	745/882	2222/3540	—	3.0	12.5	0.48/1.56	—	98
Gasoline	553/536	—	—	1.4	7.6	—	—	—
Hydrogen, H_2	845/1062	2318/4010	3247/5385	4.0	74.2	2.83/9.3	—	57
Hydrogen sulfide, H_2S	565/558	—	—	4.3	45.5	—	—	—
Mapp gas, (allene) C_3H_4	728/850	—	3200/5301	3.4	10.8	—	4.69/15.4	—
Methane, CH_4	905/1170	2191/3484	—	5.0	15.0	0.45/1.48	4.50/14.76	90
Methanol, CH_3OH	658/725	2177/3460	—	6.7	36.0	—	0.49/1.6	—
Natural gas	—	2214/3525	2916/4790	4.3	15.0	0.30/1.00	4.63/15.2	100
Producer gas	—	1927/3010	—	17.0	73.7	0.26/0.85	—	90
Propane, C_3H_8	739/871	2240/3573	3105/5130	2.1	10.1	0.46/1.52	3.72/12.2	94
Propane, commercial	773/932	2240/3573	—	2.37	9.50	0.85/2.78	—	—
Propylene, C_3H_6	—	—	3166/5240	—	—	—	—	—
Town gas (brown coal)	643/700	2318/3710	—	4.8	31.0	—	—	—

*For combustion with air at standard temperature and pressure. These flame temperatures are calculated for 100 percent theoretical air, disassociation considered. Data from *Gas Engineers Handbook,* Industrial Press, New York, 1965.

†Flame temperatures are theoretical—calculated for stoichiometric ratio, dissociation considered.

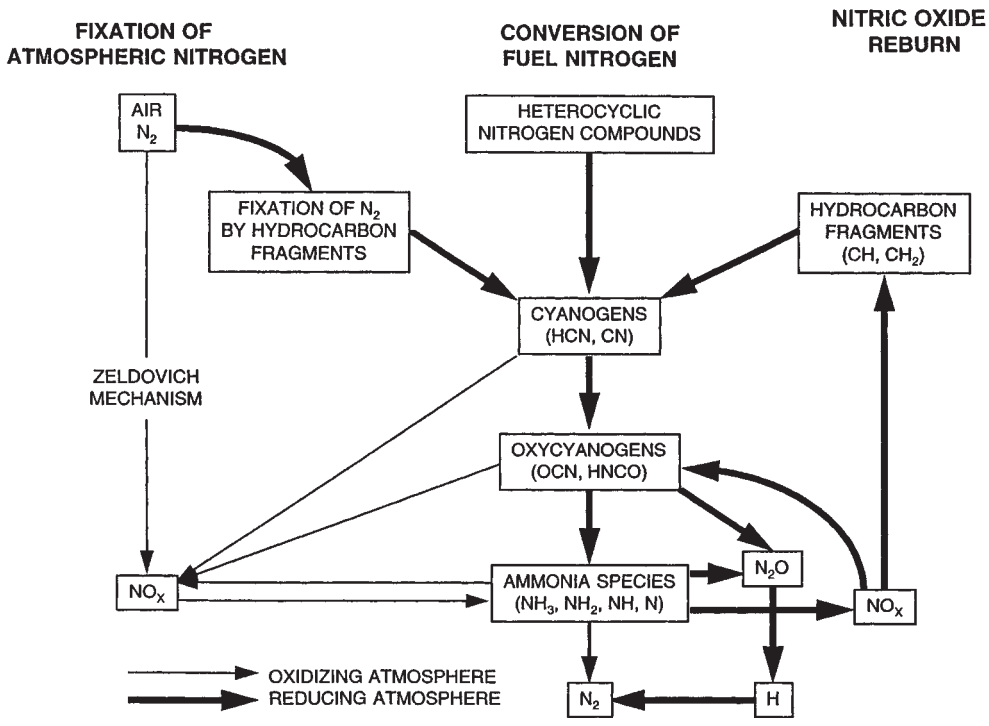


FIG. 27-14 Nitrogen oxide formation pathways in combustion.

used to refer to NO + NO_2. NO is the primary form in combustion products [typically 95 percent of total NO_x]. NO is subsequently oxidized to NO_2 in the atmosphere.)

Thermal NO_x The formation of thermal NO_x is described by the Zeldovich mechanism:

$$N_2 + O \rightleftharpoons NO + N \tag{27-42}$$

$$N + O_2 \rightleftharpoons NO + O \tag{27-43}$$

$$N + OH \rightleftharpoons NO + H \tag{27-44}$$

The first of these reactions is the rate-limiting step. Assuming that O and O_2 are in partial equilibrium, the NO formation rate can be expressed as follows:

$$\frac{d[NO]}{dt} = A[N_2][O_2]^{1/2} \exp\left(\frac{-E}{RT}\right) \tag{27-45}$$

As indicated, the rate of NO formation increases exponentially with temperature, and, of course, oxygen and nitrogen must be available for thermal NO_x to form. Thus, thermal NO_x formation is rapid in high-temperature lean zones of flames.

Fuel NO_x Fuel-bound nitrogen (FBN) is the major source of NO_x emissions from combustion of nitrogen-bearing fuels such as heavy oils, coal, and coke. Under the reducing conditions surrounding the burning droplet or particle, the FBN is converted to fixed nitrogen species such as HCN and NH_3. These, in turn, are readily oxidized to form NO if they reach the lean zone of the flame. Between 20 and 80 percent of the bound nitrogen is typically converted to NO_x, depending on the design of the combustion equipment. With prolonged exposure (order of 100 ms) to high temperature and reducing conditions, however, these fixed nitrogen species may be converted to molecular nitrogen, thus avoiding the NO formation path.

Prompt NO_x Hydrocarbon fragments (such as C, CH, CH_2) may react with atmospheric nitrogen under fuel-rich conditions to yield fixed nitrogen species such as NH, HCN, H_2CN, and CN. These, in turn, can be oxidized to NO in the lean zone of the flame. In most flames, especially those from nitrogen-containing fuels, the prompt mechanism is responsible for only a small fraction of the total NO_x. Its control is important only when attempting to reach the lowest possible emissions.

NO_x Emission Control It is preferable to minimize NO_x formation through control of the mixing, combustion, and heat-transfer processes rather than through postcombustion techniques such as selective catalytic reduction. Four techniques for doing so, illustrated in Fig. 27-15, are air staging, fuel staging, flue-gas recirculation, and lean premixing.

Air Staging Staging the introduction of combustion air can control NO_x emissions from all fuel types. The combustion air stream is split to create a fuel-rich primary zone and a fuel-lean secondary zone. The rich primary zone converts fuel-bound nitrogen to molecular nitrogen and suppresses thermal NO_x. Heat is removed prior to addition of the secondary combustion air. The resulting lower flame temperatures (below 1810 K [2800°F]) under lean conditions reduce the rate of formation of thermal NO_x. This technique has been widely applied to furnaces and boilers and it is the preferred approach for burning liquid and solid fuels. Staged-air burners are typically capable of reducing NO_x emissions by 30 to 60 percent, relative to uncontrolled levels. Air staging can also be accomplished by use of overfire air systems in boilers.

Fuel Staging Staging the introduction of fuel is an effective approach for controlling NO_x emissions when burning gaseous fuels. The first combustion stage is very lean, resulting in low thermal and prompt NO_x. Heat is removed prior to injection of the secondary fuel. The secondary fuel entrains flue gas prior to reacting, further reducing flame temperatures. In addition, NO_x reduction through reburning reactions may occur in the staged jets. This technique is the favored approach for refinery- and chemical plant–fired heaters utilizing gaseous fuels. Staged-fuel burners are typically capable of reducing NO_x emissions by 40 to 70 percent, relative to uncontrolled levels.

Flue Gas Recirculation Flue gas recirculation, alone or in combination with other modifications, can significantly reduce thermal NO_x. Recirculated flue gas is a diluent that reduces flame temperatures. External and internal recirculation paths have been applied: internal

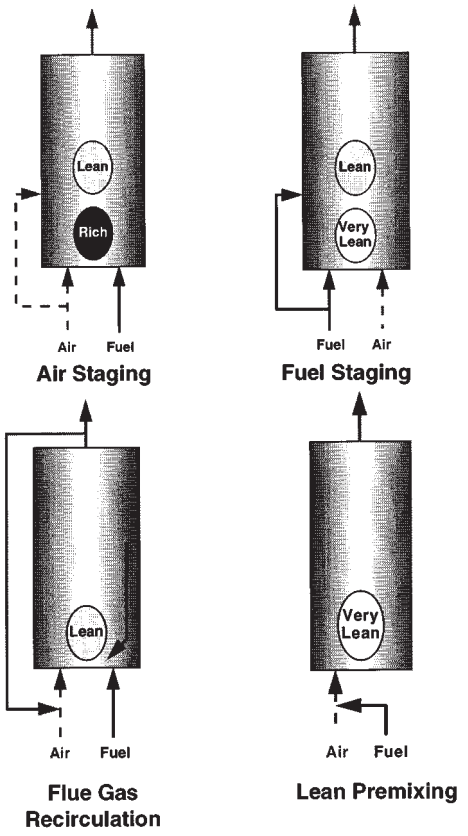


FIG. 27-15 Combustion modifications for NO_x control.

recirculation can be accomplished by jet entrainment using either combustion air or fuel jet energy; external recirculation requires a fan or a jet pump (driven by the combustion air). When combined with staged-air or staged-fuel methods, NO_x emissions from gas-fired burners can be reduced by 50 to 90 percent. In some applications, external flue-gas recirculation can decrease thermal efficiency. Condensation in the recirculation loop can cause operating problems and increase maintenance requirements.

Lean Premixing Very low NO_x emissions can be achieved by premixing gaseous fuels (or vaporized liquid fuels) with air and reacting at high excess air. The uniform and very lean conditions in such systems favor very low thermal and prompt NO_x. However, achieving such low emissions requires operating near the lean stability limit. This is an attractive NO_x control approach for gas turbines, where operation at high excess air does not incur an efficiency penalty. In this application, NO_x emissions have been reduced by 75 to 95 percent.

Sulfur Oxides Sulfur occurs in fuels as inorganic minerals (primarily pyrite, FeS_2), organic structures, sulfate salts, and elemental sulfur. Sulfur contents range from parts per million in pipeline natural gas, to a few tenths of a percent in diesel and light fuel oils, to 0.5 to 5 percent in heavy fuel oils and coals. Sulfur compounds are pyrolized during the volatilization phase of oil and coal combustion and react in the gas phase to form predominantly SO_2 and some SO_3. Conversion of fuel sulfur to these oxides is generally high (85 to 90 percent) and is relatively independent of combustion conditions. From 1 to 4 percent of the SO_2 is further oxidized to SO_3, which is highly reactive and extremely hygroscopic. It combines with water to form sulfuric acid aerosol, which can increase the visibility of stack plumes. It also elevates the dew point of water so that, to avoid back-end condensation and resulting corrosion, the flue-gas discharge temperature must be raised to about 420 K (300°F), reducing heat recovery and thermal efficiency. This reaction is enhanced by the presence of fine particles, which serve as condensation nuclei. Some coals may contain ash with substantial alkali content. In combustion of these fuels, the alkali may react to form condensed phase compounds (such as sulfates), thereby reducing the amount of sulfur emitted as oxides. Reductions in SO_2 emissions may be achieved either by removing sulfur from the fuel before and/or during combustion, or by postcombustion flue-gas desulfurization (wet scrubbing using limestone slurry, for example).

Particulates Combustion-related particulate emissions may consist of one or more of the following types, depending on the fuel.

Mineral matter derived from ash constituents of liquid and solid fuels can vaporize and condense as sub-micron-size aerosols. Larger mineral matter fragments are formed from mineral inclusions which melt and resolidify downstream.

Sulfate particles formed in the gas phase can condense. In addition, sulfate can become bound to metals and can be adsorbed on unburned carbon particles.

Unburned carbon includes unburned char, coke, cenospheres, and soot.

Particles of char are produced as a normal intermediate product in the combustion of solid fuels. Following initial particle heating and devolatilization, the remaining solid particle is termed *char.* Char oxidation requires considerably longer periods (ranging from 30 ms to over 1 s, depending on particle size and temperature) than the other phases of solid fuel combustion. The fraction of char remaining after the combustion zone depends on the combustion conditions as well as the char reactivity.

Cenospheres are formed during heavy oil combustion. In the early stages of combustion, the oil particle is rapidly heated and evolves volatile species, which react in the gas phase. Toward the end of the volatile-loss phase, the generation of gas declines rapidly and the droplet (at this point, a highly viscous mass) solidifies into a porous coke particle known as a *cenosphere.* This is called *initial coke.* For the heaviest oils, the initial coke particle diameter may be 20 percent larger than the initial droplet diameter. For lighter residual oils, it may be only one third of the original droplet diameter. After a short interval, the initial coke undergoes contraction to form *final coke.* Final coke diameter is ~80 percent of the initial droplet diameter for the heaviest oils. At this time the temperature of the particle is approximately 1070 to 1270 K (1470 to 1830°F). Following coke formation, the coke particles burn out in the lean zone, but the heterogeneous oxidation proceeds slowly. Final unburned carbon levels depend on a balance between the amount of coke formed and the fraction burned out. Coke formation tends to correlate with fuel properties such as asphaltene content, C:H ratio, or Conradson Carbon Residue. Coke burnout depends on combustion conditions and coke reactivity. Coke reactivity is influenced by the presence of combustion catalysts (e.g., vanadium) in the cenospheres.

Formation of *soot* is a gas-phase phenomenon that occurs in hot, fuel-rich zones. Soot occurs as fine particles (0.02 to 0.2 μm), often agglomerated into filaments or chains which can be several millimeters long. Factors that increase soot formation rates include high C:H ratio, high temperature, very rich conditions, and long residence times at these conditions. Pyrolysis of fuel molecules leads to soot precursors such as acetylene and higher analogs and various polyaromatic hydrocarbons. These condense to form very small (<2 nm) particles. The bulk of solid-phase material is generated by *surface growth*—attachment of gas-phase species to the surface of the particles and their incorporation into the particulate phase. Another growth mechanism is *coagulation,* in which particles collide and coalesce. Soot particle formation and growth is typically followed by soot oxidation to form CO and CO_2. Eventual soot emission from a flame depends on the relative balance between the soot-formation and oxidation reactions.

Carbon Monoxide Carbon monoxide is a key intermediate in the oxidation of all hydrocarbons. In a well-adjusted combustion system, essentially all the CO is oxidized to CO_2 and final emission of CO is very low indeed (a few parts per million). However, in systems which have low temperature zones (for example, where a flame impinges on a wall or a furnace load) or which are in poor adjustment (for example, an individual burner fuel-air ratio out of balance in a multiburner

installation or a misdirected fuel jet which allows fuel to bypass the main flame), CO emissions can be significant. The primary method of CO control is good combustion system design and practice.

Unburned Hydrocarbons Various unburned hydrocarbon species may be emitted from hydrocarbon flames. In general, there are two classes of unburned hydrocarbons: (1) small molecules that are the intermediate products of combustion (for example, formaldehyde) and (2) larger molecules that are formed by pyro-synthesis in hot, fuel-rich zones within flames, e.g., benzene, toluene, xylene, and various polycyclic aromatic hydrocarbons (PAHs). Many of these species are listed as Hazardous Air Pollutants (HAPs) in Title III of the Clean Air Act Amendment of 1990 and are therefore of particular concern. In a well-adjusted combustion system, emission of HAPs is extremely low (typically, parts per trillion to parts per billion). However, emission of certain HAPs may be of concern in poorly designed or maladjusted systems.

COMBUSTION OF SOLID FUELS

There are three basic modes of burning solid fuels, each identified with a furnace design specific for that mode: in suspension, in a bed at rest* on a grate (fuel-bed firing), or in a fluidized bed. Although many variations of these generic modes and furnace designs have been devised, the fundamental characteristics of equipment and procedure remain intact. They will be described briefly.

Suspension Firing Suspension firing of pulverized coal (PC) is commoner than fuel-bed or fluidized-bed firing of coarse coal in the United States. This mode of firing affords higher steam-generation capacity, is independent of the caking characteristics of the coal, and responds quickly to load changes. Pulverized coal firing accounts for approximately 55 percent of the power generated by electric utilities in the United States. It is rarely used on boilers of less than 45.4 Mg/h (100,000 lb/h) steam capacity because its economic advantage decreases with size.

A simplified model of PC combustion includes the following sequence of events: (1) on entering the furnace, a PC particle is heated rapidly, driving off the volatile components and leaving a char particle; (2) the volatile components burn independently of the coal particle; and (3) on completion of volatiles combustion, the remaining char particle burns. While this simple sequence may be generally correct, PC combustion is an extremely complex process involving many interrelated physical and chemical processes.

Devolatilization The volatiles produced during rapid heating of coal can include H_2, CH_4, CO, CO_2, and C_2-C_4 hydrocarbons, as well as tars, other organic compounds, and reduced sulfur and nitrogen species. The yield of these various fractions is a function of both heating rate and final particle temperature. The resulting char particle may be larger in diameter than the parent coal particle, owing to swelling produced by volatiles ejection. The particle density also decreases.

Char oxidation dominates the time required for complete burnout of a coal particle. The heterogeneous reactions responsible for char oxidation are much slower than the devolatilization process and gas-phase reaction of the volatiles. Char burnout may require from 30 ms to over 1 s, depending on combustion conditions (oxygen level, temperature), and char particle size and reactivity. Char reactivity depends on parent coal type. The rate-limiting step in char burnout can be chemical reaction or gaseous diffusion. At low temperatures or for very large particles, chemical reaction is the rate-limiting step. At higher temperatures boundary-layer diffusion of reactants and products is the rate-limiting step.

Pulverized-Coal Furnaces In designing and sizing PC furnaces, particular attention must be given to the following fuel-ash properties:

- Ash fusion temperatures, including the spread between initial deformation temperature and fluid temperature
- Ratio of basic (calcium, sodium, potassium) to acidic (iron, silicon, aluminum) ash constituents, and specifically iron-to-calcium ratio
- Ash content
- Ash friability

These characteristics influence furnace plan area, furnace volume, and burning zone size required to maintain steam production capacity for a given fuel grade or quality.

Coal properties influence pulverizer capacity and the sizing of the air heater and other heat-recovery sections of a steam generator. Furnace size and heat-release rates are designed to control slagging characteristics. Consequently, heat-release rates in terms of the ratio of net heat input to plan area range from 4.4 MW/m^2 (1.4×10^6 Btu/[h·ft^2]) for severely slagging coals to 6.6 MW/m^2 (2.1×10^6 Btu/[h·ft^2]) for low-slagging fuels.

The various burner and furnace configurations for PC firing are shown schematically in Fig. 27-16. The U-shaped flame, designated as *fantail vertical firing* (Fig. 27-16*a*), was developed initially for pulverized coal before the advent of water-cooled furnace walls. Because a large percentage of the total combustion air is withheld from the fuel stream until it projects well down into the furnace, this type of firing is well suited for solid fuels that are difficult to ignite, such as those with less than 15 percent volatile matter. Although this configuration is no longer used in central-station power plants, it may find favor again if low-volatile chars from coal-conversion processes are used for steam generation or process heating.

Modern central stations use the other burner-furnace configurations shown in Fig. 27-16, in which the coal and air are mixed rapidly in and close to the burner. The primary air, used to transport the pulverized coal to the burner, comprises 10 to 20 percent of the total combustion air. The secondary air comprises the remainder of the total air and mixes in or near the burner with the primary air and coal. The velocity of the mixture leaving the burner must be high enough to prevent flashback in the primary air-coal piping. In practice, this velocity is maintained at about 31 m/s (100 ft/s).

In *tangential firing* (Fig. 27-16*b*), the burners are arranged in vertical banks at each corner of a square (or nearly square) furnace and directed toward an imaginary circle in the center of the furnace. This results in the formation of a large vortex with its axis on the vertical centerline. The burners consist of an arrangement of slots one above the other, admitting, through alternate slots, primary air-fuel mixture and secondary air. It is possible to tilt the burners upward or downward, the maximum inclination to the horizontal being 30°, enabling the operator to selectively utilize in-furnace heat-absorbing surfaces, especially the superheater.

The circular burner shown in Fig. 27-17 is widely used in horizontally fired furnaces and is capable of firing coal, oil, or gas in capacities as high as 174 GJ/h (1.65×10^5 Btu/h). In such burners the air is often swirled to create a zone of reverse flow immediately downstream of the burner centerline, which provides for combustion stability.

Low-NO_x burners are designed to delay and control the mixing of coal and air in the main combustion zone. A typical low-NO_x air-staged burner is illustrated in Fig. 27-18. This combustion approach can reduce NO_x emissions from coal burning by 40 to 50 percent. Because of the reduced flame temperature and delayed mixing in a low-NO_x burner, unburned carbon emissions may increase in some applications and for some coals. *Overfire air* is another technique for staging the combustion air to control NO_x emissions when burning coal in suspension-firing systems. Overfire air ports are installed above the top level of burners on wall- and tangential-fired boilers. Use of overfire air can reduce NO_x emissions by 20 to 30 percent. *Reburn* is a NO_x control strategy that involves diverting a portion of the fuel from the burners to a second combustion zone (reburn zone) above the main burners. Completion air is added above the reburn zone to complete fuel burnout. The reburn fuel can be natural gas, oil, or pulverized coal, though natural gas is used in most applications. In this approach, the stoichiometry in the reburn zone is controlled to be slightly rich (equivalence ratio of ~1.15), under which conditions a portion (50 to 60 percent) of the NO_x is converted to molecular nitrogen.

Pulverizers The pulverizer is the heart of any solid-fuel suspen-

* The burning fuel bed may be moved slowly through the furnace by the vibrating action of the grate or by being carried on a traveling grate.

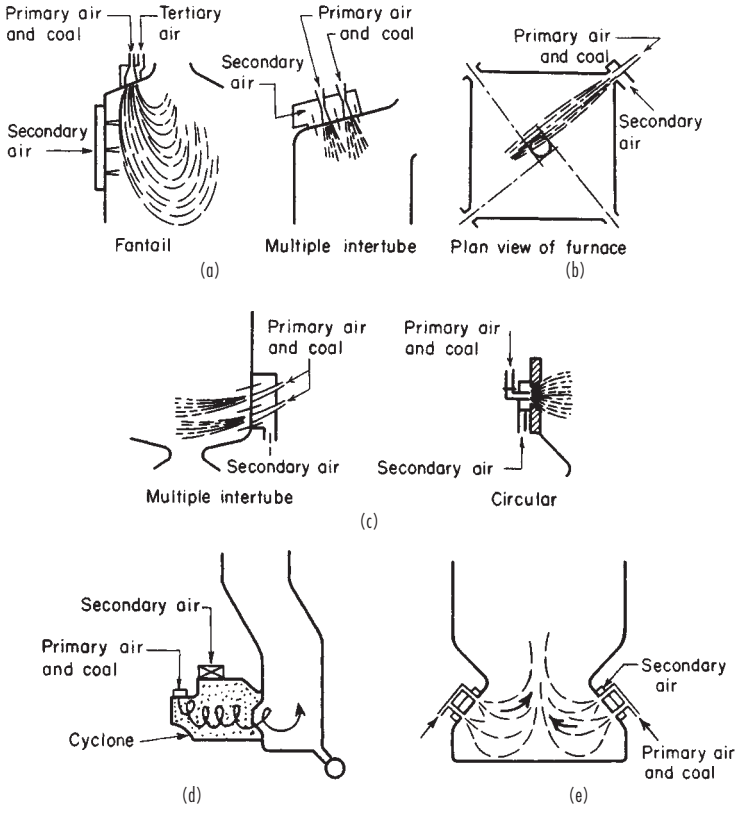


FIG. 27-16 Burner and furnace configurations for pulverized-coal firing: (*a*) vertical firing; (*b*) tangential firing; (*c*) horizontal firing; (*d*) cyclone firing; (*e*) opposed-inclined firing.

sion-firing system. Air is used to dry the coal, transport it through the pulverizer, classify it, and transport it to the burner, where the transport air provides part of the air for combustion. The pulverizers themselves are classified according to whether they are under positive or negative pressure and whether they operate at slow, medium, or high speed.

Pulverization occurs by impact, attrition, or crushing. The capacity of a pulverizer depends on the grindability of the coal and the fineness desired, as shown by Fig. 27-19. Capacity can also be seriously reduced by excessive moisture in the coal, but it can be restored by increasing the temperature of the primary air. Figure 27-20 indicates the temperatures needed. For PC boilers, the coal size usually is 65 to 80 percent through a 200-mesh screen, which is equivalent to 74 μm. Several kinds of available pulverizers and their characteristics are discussed in Sec. 20.

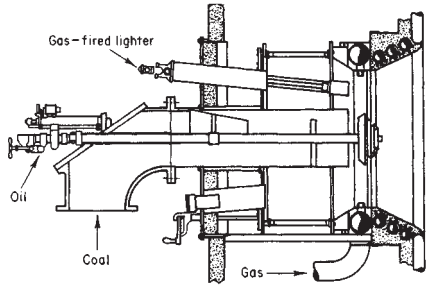


FIG. 27-17 Circular burner for pulverized coal, oil, or gas. (*From* Marks' Standard Handbook for Mechanical Engineers, *8th ed., McGraw-Hill, New York, 1978.*)

Cyclone Furnaces In *cyclone firing* (Fig. 27-16*d*) the coal is not pulverized but is crushed to 4-mesh (4.76-mm) size and admitted tangentially with primary air to a horizontal cylindrical chamber, called a *cyclone furnace*, which is connected peripherally to a boiler furnace. Secondary air also is admitted, so that almost all of the coal burns within the chamber. The combustion gas then flows into the boiler furnace. In the cyclone furnace, finer coal particles burn in suspension and the coarser ones are thrown centrifugally to the chamber wall, where most of them are captured in a sticky wall coating of molten slag. The secondary air, admitted tangentially along the top of the cyclone furnace, sweeps the slag-captured particles and completes their combustion. A typical firing rate is about 18.6 GJ/(h·m^3) (500,000 Btu/[h·ft^3]). The slag drains continuously into the boiler furnace and thence into a quenching tank. Figure 27-21 shows a cyclone furnace schematically.

Fuel-Bed Firing Fuel-bed firing is accomplished with mechanical stokers, which are designed to achieve continuous or intermittent fuel feed, fuel ignition, proper distribution of the combustion air, free release of the gaseous combustion products, and continuous or intermittent disposal of the unburned residue. These aims are met with two classes of stokers, distinguished by the direction of fuel feed to the bed: underfeed and overfeed. Overfeed stokers are represented by two types, distinguished by the relative directions of fuel and air flow (and also by the manner of fuel feed): crossfeed, also termed mass-burning, and spreader. The principles of these three methods of fuel-bed firing are illustrated schematically in Fig. 27-22.

Underfeed Firing Both fuel and air have the same relative

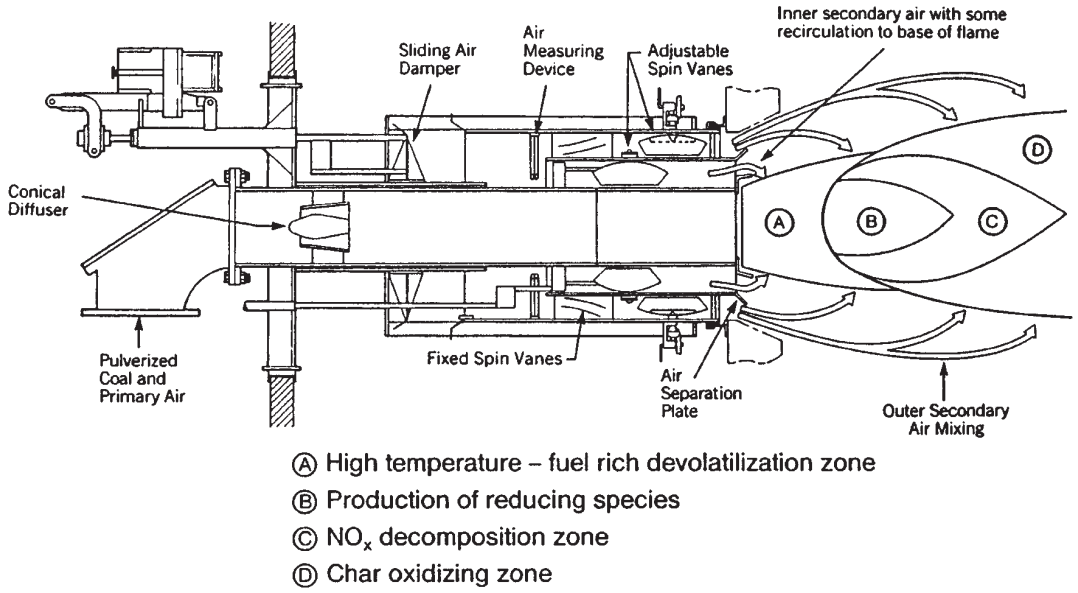


FIG. 27-18 Low-NO_x pulverized coal burner. (*Babcock & Wilcox Co.*)

direction in the underfeed stoker, which is built in single-retort and multiple-retort designs. In the *single-retort,* side-dump stoker, a ram pushes coal into the retort toward the end of the stoker and upward toward the tuyere blocks, where air is admitted to the bed. This type of stoker will handle most bituminous coals and anthracite, preferably in the size range 19 to 50 mm (¾ to 2 in) and no more than 50 percent through a 6-mm (¼-in) screen. Overfire air or steam jets are frequently used in the bridgewall at the end of the stoker to promote turbulence.

In the *multiple-retort stoker,* rams feed coal to the top of sloping grates between banks of tuyeres. Auxiliary small sloping rams perform

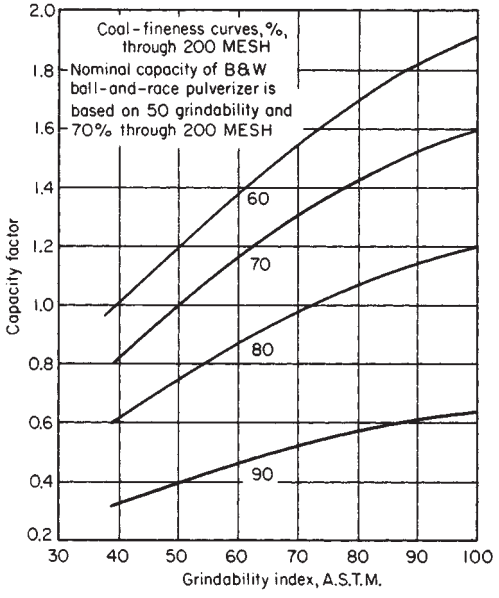


FIG. 27-19 Variation of pulverizer capacity with the grindability of the coal and the fineness to which the coal is ground. (*Babcock & Wilcox Co.*)

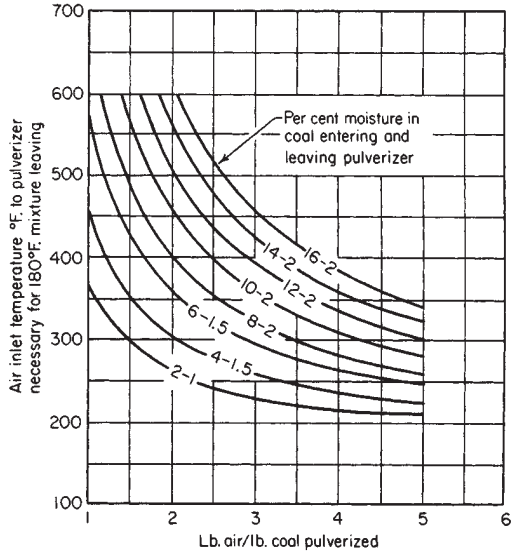


FIG. 27-20 Effect of moisture in coal on pulverizer capacity. Sufficient drying can be accomplished to restore capacity if air temperatures are high enough. [K = (°F + 459.7)/1.8] (Combustion Engineer, *Combustion Engineering Inc., New York, 1966.*)

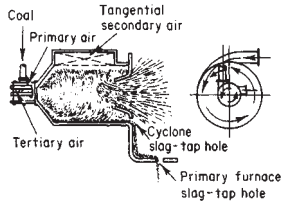


FIG. 27-21 Cyclone furnace. (*From* Marks' Standard Handbook for Mechanical Engineers, *9th ed., McGraw-Hill, New York, 1987.*)

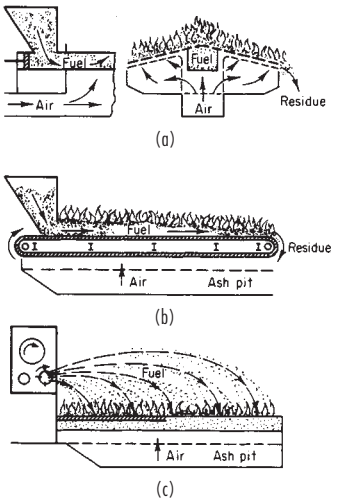


FIG. 27-22 Basic types of mechanical stokers: (*a*) underfeed; (*b*) crossfeed; (*c*) overfeed (spreader stoker).

the same function as the pusher rods in the single retort. Air is admitted along the top of the banks of tuyeres, and on the largest units the tuyeres themselves are given a slight reciprocating action to agitate the bed further. This type of stoker operates best with caking coals having a relatively high ash-softening temperature. Coal sizing is up to 50 mm (2 in) with 30 to 50 percent through a 6-mm (¼-in) screen.

Overfeed Firing: Crossfeed (Mass-Burning) Stokers Crossfeed stokers are also termed mass-burning stokers because the fuel is dumped by gravity from a hopper onto one end of a moving grate, which carries it into the furnace and down its length. Because of this feature, crossfeed stokers are commonly called *traveling-grate* stokers. The grate may be either of two designs: *bar grate* or *chain grate.* Alternatively, the burning fuel bed may be conveyed by a vibratory motion of the stoker (*vibrating-grate*).

The fuel flows at right angles to the air flow. Only a small amount of air is fed at the front of the stoker, to keep the fuel mixture rich, but as the coal moves toward the middle of the furnace, the amount of air is increased, and most of the coal is burned by the time it gets halfway down the length of the grate. Fuel-bed depth varies from 100 to 200 mm (4 to 8 in), depending on the fuel, which can be coke breeze, anthracite, or any noncaking bituminous coal.

Overfeed Firing: Spreader Stokers Spreader stokers burn coal (or other fuel) by propelling it into the furnace. A portion of the coal burns in suspension (the percentage depending on the coal fineness), while the rest burns on a grate. In most units, coal is pushed off a plate under the storage hopper onto revolving paddles (either overthrow or underthrow) which distribute the coal on the grate (Fig. 27-22*c*). The angle and speed of the paddles control coal distribution. The largest coal particles travel the farthest, while the smallest ones become partially consumed during their trajectory and fall on the forward half of the grate. The grate may be stationary or traveling. The fuel and air flow in opposite directions.

Some spreaders use air to transport the coal to the furnace and distribute it, while others use mechanical means to transport the coal to a series of pneumatic jets.

The performance of spreader stokers is affected by changes in coal sizing. The equipment can distribute a wide range of fuel sizes, but it distributes each particle on the basis of size and weight. Normal size specifications call for 19-mm (¾-in) nut and slack with not more than 30 percent less than 6.4 mm (¼ in).

Typically, approximately 30 to 50 percent of the coal is burned in suspension. If excessive fines are present, more coal particles will be carried out of the furnace and burned in suspension, and very little ash will be available to provide a protective cover for the grate surface. On the other hand, if sufficient fines are not present, not all the fuel will be burned on the grate, resulting in derating of the unit and excessive dumping of live coals to the ash hopper.

Excess air is usually 30 to 40 percent for stationary and dumping grates, while traveling grates are operated with from 22 to 30 percent excess air. Preheated air can be supplied for all types of grates but the temperature is usually limited to 395 to 422 K (250 to 300°F) to prevent excessive slagging of the fuel bed.

Overfire air nozzles are located in the front wall underneath the spreaders and in the rear wall from 0.3 to 0.9 m (1 to 3 ft) above the grate level. These nozzles use air directly from a fan or inspirate air with steam to provide turbulence above the grate for most effective mixing of fuel and air. They supply about 15 percent of the total combustion air.

Comparison of Suspension and Fuel-Bed Firing A major factor to consider when comparing a stoker-fired boiler with a PC boiler is the reduction in efficiency due to carbon loss. The carbon content of the ash passing out of a spreader stoker furnace varies from 30 to 50 percent. Overall efficiency of the stoker can be increased by reburning the ash: it is returned to the stoker grate by gravity or a pneumatic feed system. A continuous-ash-discharge spreader-stoker-fired unit will typically have a carbon loss of 4 to 8 percent, depending on the amount of ash reinjection. A properly designed PC boiler, on the other hand, can maintain an efficiency loss due to unburned carbon of less than 0.4 percent.

A difference between these firing methods may also be manifested in the initial fuel cost. For efficient operation of a spreader-stoker-fired boiler, the coal must consist of a proper mixture of coarse and fine particles. Normally, double-screened coal is purchased because less expensive run-of-mine coal does not provide the optimum balance of coarse and fine material.

An advantage of a stoker-fired furnace is its easy adaptability to firing almost any unsized solid fuels. Bark, bagasse, or refuse can normally be fired on a stoker to supplement the coal with a minimum amount of additional equipment. Thus, such supplementary waste fuels may be able to contribute a higher percentage of the total heat input in a stoker-fired furnace than in a PC furnace without expensive equipment modifications.

Fluidized-Bed Combustion The principles of gas-solid fluidization and their application to the chemical process industry are treated in Section 17. Their general application to combustion is reviewed briefly here, and their more specific application to fluidized-bed boilers is discussed later in this section.

In fluidized-bed combustion (FBC) fuel is burned in a bed of particles supported in an agitated state by an upward flow of air introduced via an air distributor. The bed particles may be sand or ash derived from the fuel, but usually they are a sulfur sorbent, like limestone or dolomite. Fluidized beds have inherently good heat-transfer characteristics, and these ensure even temperatures within the combustor and high flux rates to steam/water cooling circuits. The good gas-solids contacting promotes effective sulfur capture and allows high combustion efficiency to be achieved at temperatures significantly lower than those of a pulverized coal furnace (typically 1116 K [1550°F] compared to over 1589 K [2400°F]). These lower temperatures also result in reduced slagging and fouling problems and significantly lower NO_x formation. This latter benefit, in conjunction with the reduced SO_2 emissions, constitutes one of the great advantages of fluidized-bed combustors: in situ pollution control. Having this control built into the furnace eliminates the need for back-end cleanup and reduces plant capital cost while increasing thermal efficiency.

There are two types of FBC unit distinguished by their operating flow characteristics: *bubbling* and *circulating.* These two types operate at atmospheric pressure, AFBC, or at elevated pressure, PFBC. Pressures for PFBC are in the range 0.6 to 1.6 MPa (90 to 240 psia). Typical superficial fluidizing velocities are tabulated as follows.

	Atmospheric	Pressurized
Bubbling	1.5–2.7 m/s (5–9 ft/s)	1–1.2 m/s (3–4 ft/s)
Circulating	3.7–7.3 m/s (12–24 ft/s)	3.7–4.3 m/s (12–14 ft/s)

Bubbling Beds In bubbling beds a large proportion of the noncombustible feedstock, mainly sorbent derived, remains in the combustor, forming the bed. Bed depth is maintained by draining off excess material. Most of the gas in excess of that required for minimum fluidization appears as bubbles (voids), and these carry particles upward in their wake, promoting the rapid vertical mixing within the bed that results in the even temperatures characteristic of FBC units. Bed temperature is controlled by heat transfer to in-bed boiler tubes and/or to the water-wall tubes used to enclose the furnace. Some units have experienced metal loss from these tube surfaces, a combined effect of erosion and abrasion, and suitable protection needs to be provided. Protective measures include surface coatings such as plasma-sprayed metal coatings incorporating silicon carbide, and metal fins to disrupt the solids-flow pattern.

In AFBC units, heat is removed from the flue gas by a convection-pass tube bank. The particulates leaving the boiler with the flue gas consist of unreacted and spent sorbent, unburned carbon, and ash. Multiclones after the convection pass remove much of the particulate matter and recycle it to the combustor, increasing the in-furnace residence time and improving combustion efficiency and sulfur retention performance. Bubbling PFBC units do not have convection-pass tube banks and do not recycle solids to the boiler.

Circulating Beds These fluidized beds operate at higher velocities, and virtually all the solids are elutriated from the furnace. The majority of the elutriated solids, still at combustion temperature, are captured by reverse-flow cyclone(s) and recirculated to the foot of the combustor. This recycle stage is incorporated into AFBC and PFBC units, but only the AFBC unit has a convection pass downstream of the cyclone. The foot of the combustor is a potentially very erosive region, as it contains large particles not elutriated from the bed, and they are being fluidized at high velocity. Consequently, the lower reaches of the combustor do not contain heat-transfer tubes and the water walls are protected with refractory. Some combustors have experienced damage at the interface between the water walls and the refractory, and measures similar to those employed in bubbling beds have been used to protect the tubes in this region.

The furnace temperature is controlled by heat transfer through the exposed upper water-wall tubes. As the units increase in size, more heat-transfer surface is required than is provided by the walls. Surface can be added by wrapping horizontal tubing over the walls of the upper furnace, or by added *wing walls,* sections of water wall extending short distances into the furnace enclosure. In some designs, tubes are extended across the upper furnace where, although the fluidizing velocity is still high, the erosion potential is low because the solids are finer and their concentration is lower. In some designs, heat is removed from the recirculated solids by passing them through a bubbling-bed heat exchanger before returning them to the furnace.

In the bubbling version, all the air is introduced through the distributor plate, but for the circulating units, 30 to 40 percent is introduced above the distributor. This staged entry results in the lower reaches operating substoichiometrically, which helps to reduce NO_x emissions but tends to reduce the fluidizing velocity at the base of the combustor. To compensate for this and increase the mixing by increasing the local gas velocity, the portion of the combustor below the secondary air entry points is tapered. Staging is not generally employed on bubbling units because the oxygen deficiency in the bed tends to accelerate corrosion of the in-bed tube bank.

Fuel Flexibility An advantage of FBC designs is fuel flexibility: a single unit can burn a wider range of fuels than a PC furnace, thus offering owners an improved bargaining position to negotiate lower fuel prices. Among the fuels fired are bituminous and subbituminous coals, anthracite culm, lignite, petroleum coke, refuse-derived fuel, biomass, industrial and sewage sludges, and shredded tires. But fuel flexibility can be achieved only if the unit is designed for the range of fuels intended to be burned. For example, to maintain the same firing rate, a feed system designed for a certain fuel must be capable of feeding a lower calorific fuel at a higher rate. Similarly, to maintain the same degree of sulfur capture, feeders must be capable of delivering sorbent over a range of rates matching the sulfur contents of the fuels likely to be fed.

Sulfur Emissions Sulfur present in a fuel is released as SO_2, a known contributor to acid rain deposition. By adding limestone or dolomite to a fluidized bed, much of this can be captured as calcium sulfate, a dry nonhazardous solid. As limestone usually contains over 40 percent calcium, compared to only 20 percent in dolomite, it is the preferred sorbent, resulting in lower transportation costs for the raw mineral and the resulting ash product. Moreover, the high magnesium content of the dolomite makes the ash unsuitable for some building applications and so reduces its potential for utilization. Whatever sorbent is selected, for economic reasons it is usually from a source local to the FBC plant. If more than one sorbent is available, plant trials are needed to determine the one most suitable, as results from laboratory-scale reactivity assessments are unreliable.

At atmospheric pressure, calcium carbonate almost completely calcines to free lime, and it is this that captures the sulfur dioxide. As the free lime is not completely sulfated, the resulting sorbent ash is very alkaline, consisting primarily of $CaSO_4$ and CaO, with small amounts of $CaCO_3$.

$$CaCO_3 \rightleftharpoons CaO + CO_2 \tag{27-46}$$

$$CaO + SO_2 + [O] \rightleftharpoons CaSO_4 \tag{27-47}$$

The sulfation reaction has an optimum at a mean bed temperature of around 1116 K (1550°F).

At elevated pressure, the partial pressure of carbon dioxide inhibits calcination, and sulfur dioxide is captured by displacement of the carbonate radical. The overall effect is similar except, as no free lime is formed, the resulting sorbent ash is less alkaline, consisting solely of $CaSO_4$ and $CaCO_3$.

$$CaCO_3 + SO_2 + [O] \rightleftharpoons CaSO_4 + CO_2 \tag{27-48}$$

The sulfation reaction does not have an optimum reaction temperature under pressurized operating conditions and the higher partial pressure of oxygen results in increased conversion of sulfur dioxide to sulfur trioxide.

$$SO_2 + [O] \rightleftharpoons SO_3 \tag{27-49}$$

Under normal operating conditions, the concentration of the trioxide is unlikely to exceed 10 ppmv, but this is sufficient to elevate the acid dew point to around 422 K (300°F). This places a limit on the lowest acceptable back-end temperature if acid condensation and resulting corrosion problems are to be avoided.

Nitrogen Oxide Emissions FBC units achieve excellent combustion and sulfur emission performance at relatively modest combustion temperatures in the range 1060 to 1172 K (1450 to 1650°F). At these temperatures no atmospheric nitrogen is converted to NO_x and only a small percentage of the fuel nitrogen is converted. Typical NO_x emissions, consisting of around 90 percent NO and 10 percent NO_2, are in the range 86 to 129 mg/MJ (0.2 to 0.3 lb/10^6 Btu). In circulating AFBCs and in bubbling PFBCs, these values have been reduced to as low as 21 mg/MJ (0.05 lb/10^6 Btu) by injecting ammonia into the boiler freeboard to promote selective noncatalytic reduction (SNCR) reactions. In AFBC units, the prime variables influencing NO_x formation are excess air, mean bed temperature, the nitrogen content of the fuel, and the Ca/S molar ratio. With respect to the latter, high sorbent feed rates increase the free lime content, which catalyzes NO_x formation. In PFBC units, only excess air and fuel nitrogen content have an influence, and there appears to be no effect of pressure.

Particulate Emissions To meet environmental regulations, AFBC boilers, and some PFBC boilers, use a back-end particulate collector, such as a baghouse or an electrostatic precipitator (ESP). Compared to PC units, the ash from FBCs has higher resistivity and is finer because the flue-gas path contains cyclones. Both factors result in reduced ESP collection efficiency with AFBC units, but good performance has been achieved with PFBC units, where the SO_3 present in the flue gas lowers the ash resistivity. In general, however, baghouses are the preferred collection devices for both AFBC and PFBC applications.

FBC ash is irregular, whereas PC ash, because it melts at the elevated operating temperatures, is spherical. This difference in shape influences baghouse design in three ways: (1) FBC ash does not flow

from the collection hoppers as readily and special attention has to be given to their design; (2) FBC ash forms a stronger cake, requiring more frequent and more robust cleaning mechanisms, e.g., shake-deflate and pulse-jet technologies; and (3) this more robust action in conjunction with the more abrasive, irregular particles results in filter bags being more prone to failure in FBC systems. Careful selection of bag materials (synthetic felts generally perform best) and good installation and maintenance practices minimize the latter problem.

Some PFBC boiler designs incorporate high-temperature, high-pressure (HTHP) filter devices in the flue-gas stream. These are installed primarily to protect the gas turbine from erosion damage by the fine particles that escape the cyclones, but as the filters remove virtually all the suspended particulates, they also eliminate the need for back-end removal. The commonest HTHP filter elements used are rigid ceramic candles.

COMBUSTION OF LIQUID FUELS

Oil is typically burned as a suspension of droplets generated by atomizing the fuel. As the droplets pass from the atomizer into the flame zone, they are heated both by radiation from the flame and by convection from the hot gases that surround them, and the lighter fuel components vaporize. The vapors mix with surrounding air and ignite. Depending on the fuel type, the fuel droplet may be completely vaporized or it may be partially vaporized, leaving a residual char or coke particle.

Fuel oils can contain a significant amount of sulfur: in the case of high-sulfur No. 6, it may be as much as 4 percent (Table 27-6). SO_2 is the principal product of sulfur combustion with stoichiometric or leaner fuel-air mixtures, but with the excess air customarily used for satisfactory combustion, SO_3 can form and then condense as sulfuric acid at temperatures higher than the normally expected dew point. Thus air preheaters and other heat recovery equipment in the flue-gas stream can be endangered. Figure 27-23 shows the maximum safe upper limits for dew points in the stacks of furnaces burning sulfur-containing oil and emitting unscrubbed flue gas.

Atomizers Atomization is the process of breaking up a continuous liquid phase into discrete droplets. Figure 27-24 shows the idealized process by which the surface area of a liquid sheet is increased until it forms droplets. Atomizers may be classified into two broad groups (see Fig. 27-25): pressure atomizers, in which fuel oil is injected at high pressure, and twin-fluid atomizers, in which fuel oil is injected at moderate pressure and a compressible fluid (steam or air) assists in the atomization process. Low oil viscosity (less than 15 mm^2/s) is required for effective atomization (i.e., small droplet size). Light oils, such as No. 2 fuel oil, may be atomized at ambient temperature. However, heavy oils must be heated to produce the desired viscosity.

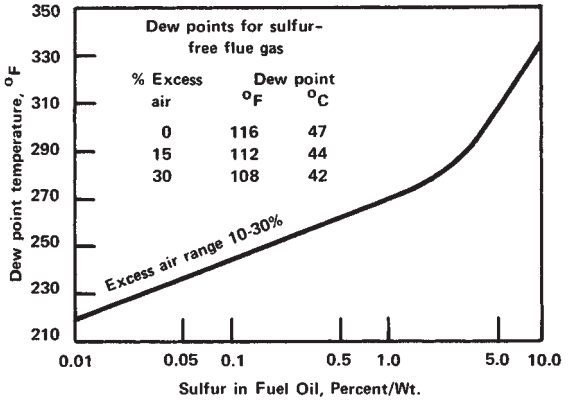


FIG. 27-23 Maximum flue-gas dew point versus percent of sulfur in typical oil fuels. (K = [°F + 459.7]/1.8)

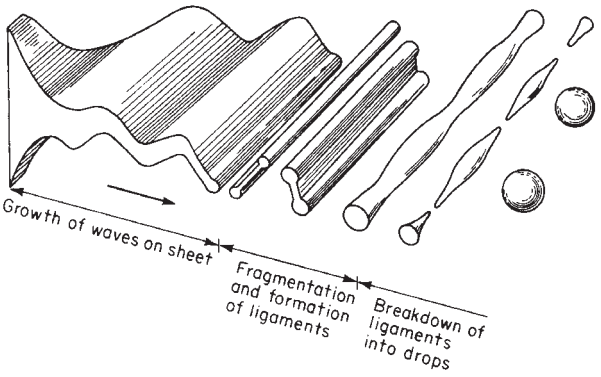


FIG. 27-24 Idealized process of drop formation by breakup of a liquid sheet. (*After Dombrowski and Johns,* Chem. Eng. Sci. ***18:*** *203, 1963.*)

Required preheats vary from approximately 373 K (212°F) for No. 6 oil to 623 K (480°F) for vacuum bottoms.

Pressure Atomizers The commonest type of pressure atomizer is the swirl-type (Fig. 27-26). Entering a small cup through tangential orifices, the oil swirls at high velocity. The outlet forms a dam around the open end of the cup, and the oil spills over the dam in the form of a thin conical sheet, which subsequently breaks up into thin filaments and then droplets. Depending on the fuel viscosity, operating pressures range from 0.69 to 6.9 MPa (100 to 1000 psia) and the attainable turndown ratio is approximately 4:1. Pressure atomization is most effective for lighter fuel oils.

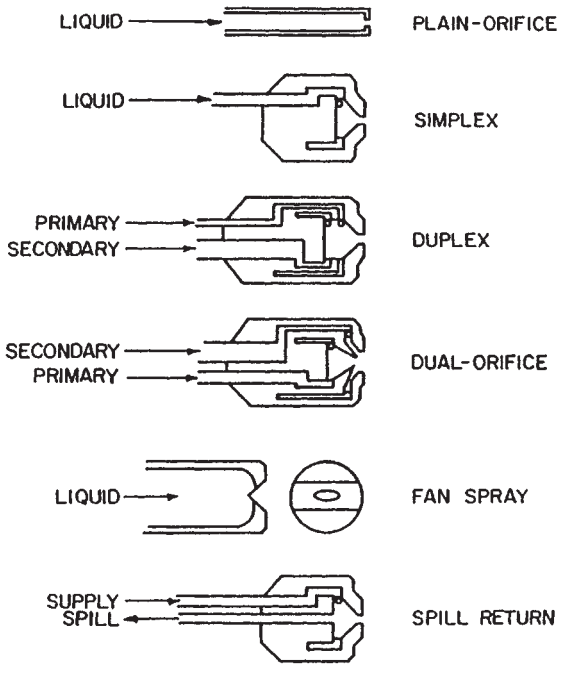


FIG. 27-25*a* Common types of atomizers: pressure atomizers. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

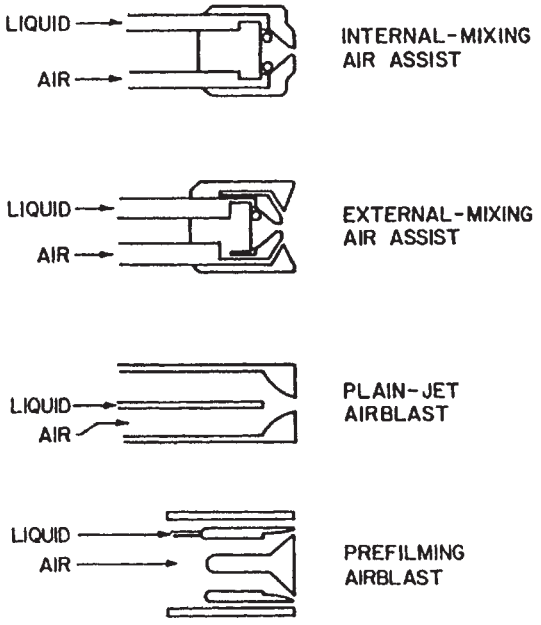


FIG. 27-25*b* Common types of atomizers: twin-fluid atomizers. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

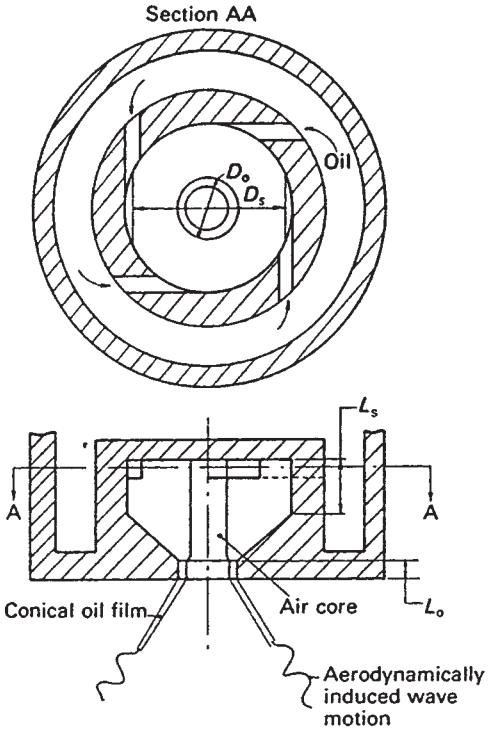


FIG. 27-26 Swirl pressure-jet atomizer. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

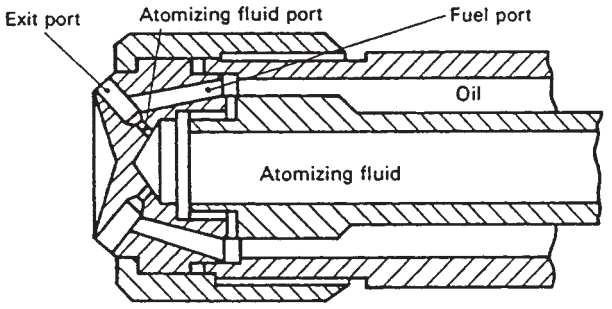


FIG. 27-27 Y-jet twin-fluid atomizer. (*From Lefebvre,* Atomization and Sprays, *Hemisphere, New York, 1989. Reproduced with permission. All rights reserved.*)

Twin-Fluid Atomizers In a twin-fluid atomizer, the fuel stream is exposed to a stream of air or steam flowing at high velocity. In the internal-mixing configuration (Fig. 27-27), the liquid and gas mix inside the nozzle before discharging through the outlet orifice. In the external-mixing nozzle, the oil stream is impacted by the high-velocity gas stream outside the nozzle. The internal type requires lower flows of secondary fluid. In industrial combustion systems, steam is the preferred atomizing medium for these nozzles. In gas turbines, compressed air is more readily available. Maximum oil pressure is about 0.69 MPa (100 psia), with the steam or air pressure being maintained about 0.14 to 0.28 MPa (20 to 40 psia) in excess of the oil pressure. The mass flow of atomizing fluid varies from 5 to 30 percent of the fuel flow rate, and represents only a modest energy consumption. Turndown performance is better than for pressure atomizers and may be as high as 20:1.

A well-designed atomizer will generate a cloud of droplets with a mean size of about 30 to 40 μm and a top size of about 100 μm for light oils such as No. 2 fuel oil. Mean and top sizes are somewhat larger than this for heavier fuel oils.

Oil Burners The structure of an oil flame is shown in Fig. 27-28, and Fig. 27-29 illustrates a conventional circular oil burner for use in boilers. A combination of stabilization techniques is used, typically including swirl. It is important to match the droplet trajectories to the combustion aerodynamics of a given burner to ensure stable ignition and good turndown performance.

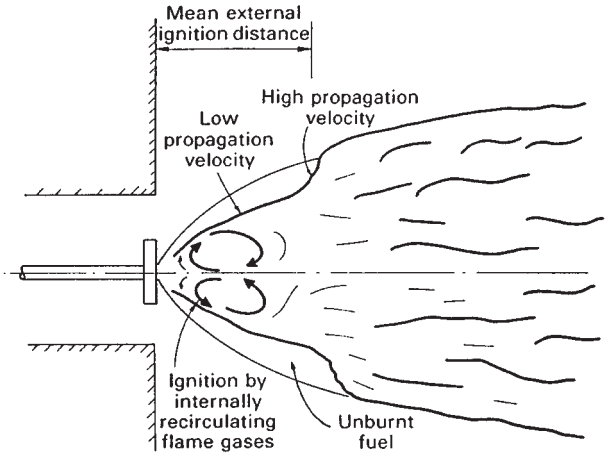


FIG. 27-28 Structure of typical oil flame. (*From Lawn,* Principles of Combustion Engineering for Boilers, *Academic Press, London, 1987. Reprinted with permission.*)

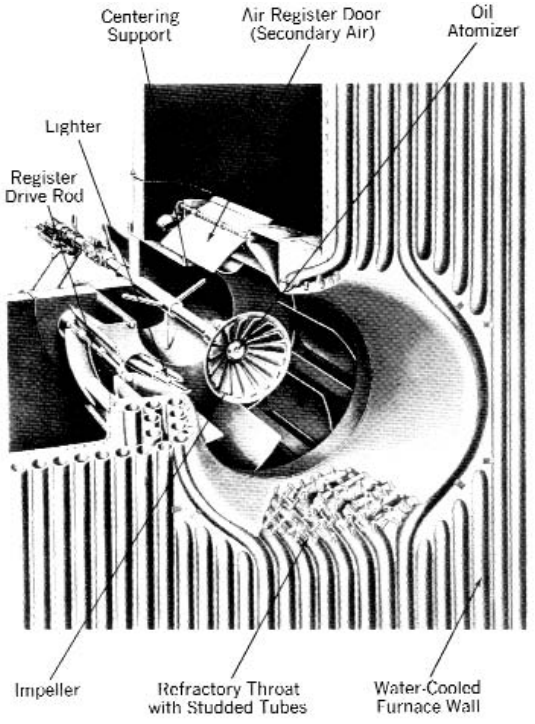


FIG. 27-29 Circular register burner with water-cooled throat for oil firing. (*Babcock & Wilcox Co.*)

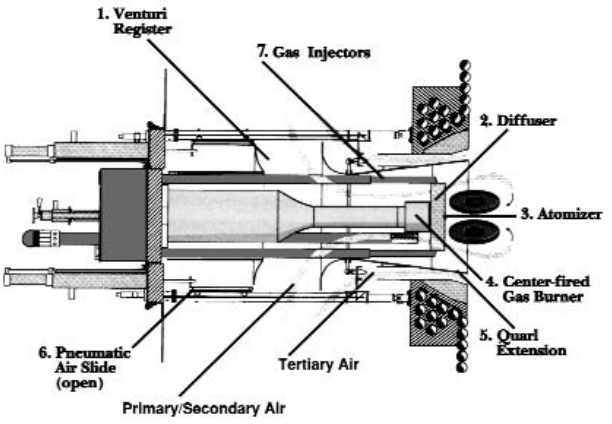


FIG. 27-30 Low-NO_x combination oil/gas forced-draft boiler burner. (*Todd Combustion, Inc.*)

Many oil burners are designed as combination gas/oil burners. An example of a modern low-NO_x oil/gas forced-draft burner is shown in Fig. 27-30. This is an air-staged design, with the air divided into primary, secondary, and tertiary streams. An air-staged natural draft process heater oil/gas burner is illustrated in Fig. 27-31.

Emissions of unburned carbon (primarily coke cenospheres) may be reduced by (1) achieving smaller average fuel droplet size (e.g., by heating the fuel to lower its viscosity or by optimizing the atomizer geometry), (2) increasing the combustion air preheat temperature, or (3) firing oils with high vanadium content (vanadium appears to catalyze the burnout of coke).

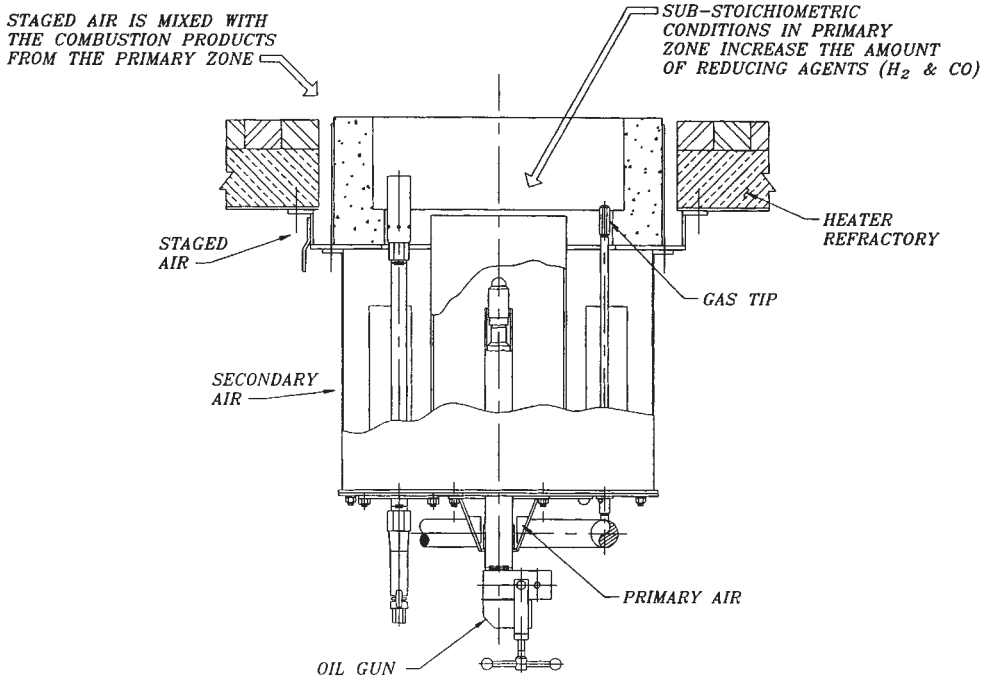


FIG. 27-31 Air-staged natural-draft combination oil/gas burner. (*Callidus Technologies, Inc.*)

COMBUSTION OF GASEOUS FUELS

Combustion of gas takes place in two ways, depending upon when gas and air are mixed. When gas and air are mixed before ignition, as in a Bunsen burner, burning proceeds by hydroxylation. The hydrocarbons and oxygen form hydroxylated compounds that become aldehydes; the addition of heat and additional oxygen breaks down the aldehydes to H_2, CO, CO_2, and H_2O. Inasmuch as carbon is converted to aldehydes in the initial stages of mixing, no soot can be developed even if the flame is quenched.

Cracking occurs when oxygen is added to hydrocarbons after they have been heated, decomposing the hydrocarbons into carbon and hydrogen, which, when combined with sufficient oxygen, form CO_2 and H_2O. Soot and carbon black are formed if insufficient oxygen is present or if the combustion process is arrested before completion.

Gas Burners Gas burners may be classified as premixed or nonpremixed. Many types of flame stabilizer are employed in gas burners (see Fig. 27-32). Bluff body, swirl, and combinations thereof are the predominant stabilization mechanisms.

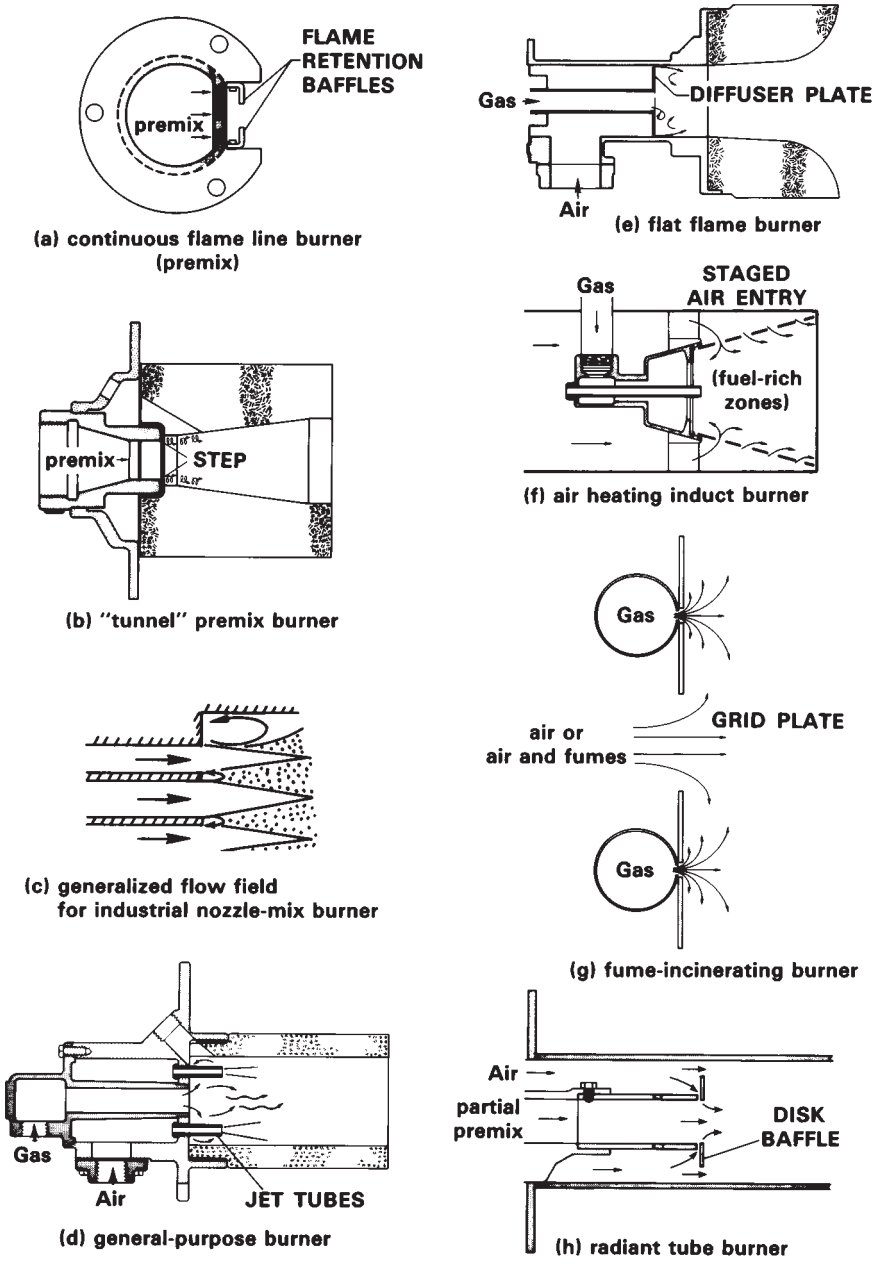


FIG. 27-32 Flame-holding arrangements. Cases (*a*) through (*f*) are various forms of bluff bodies, creating recirculation and fine-scale turbulence in their wake. Cases (*d*) through (*g*) constitute air jets blasting through a relatively quiescent volume of raw gas. Case (*f*) may be cylindrical, as in a gas turbine burner, or trough-like. (*From* North American Combustion Handbook, *3d ed., North American Manufacturing Company, Cleveland, 1996.*)

Fully Premixed Burners A fully premixed burner includes a section for completely mixing the fuel and air upstream of the burner. The burner proper consists essentially of a flame holder; see for example, Fig. 27-32*a, b*. The porting that admits the mixture to the combustion chamber is designed to produce a fairly high velocity through a large number of orifices to avoid the possibility of the flame flashing back through the flame holder and igniting the mixture upstream of the burner.

Surface combustion devices are designed for fully premixing the gaseous fuel and air and burning it on a porous radiant surface. The close coupling of the combustion process with the burner surface results in low flame temperatures and, consequently, low NO_x formation. Surface materials can include ceramic fibers, reticulated ceramics, and metal alloy mats. This approach allows the burner shape to be customized to match the heat transfer profile with the application.

Partially Premixed Burners These burners have a premixing section in which a mixture that is flammable but overall fuel-rich is generated. Secondary combustion air is then supplied around the flame holder. The fuel gas may be used to aspirate the combustion air or vice versa, the former being the commoner. Examples of both are provided in Figs. 27-33 and 27-34.

Nozzle-Mix Burners The most widely used industrial gas burners are of the nozzle-mix type. The air and fuel gas are separated until they are rapidly mixed and reacted after leaving the ports. Figure 27-32*c, d, e, f, h* shows some examples of the variety of nozzle-mix designs in use. These burners allow a wide range of fuel-air ratios, a wide variety of flame shapes, and multifuel firing capabilities. They can be used to generate special atmospheres by firing at very rich conditions (50 percent excess fuel) or very lean conditions (1000 percent excess air). By changing nozzle shape and degree of swirl, the flame profile and mixing rates can be varied widely, from a rapid-mixing short flame ($L/D = 1$), to a conventional flame ($L/D = 5$ to 10), to a slow-mixing long flame ($L/D = 20$ to 50).

Staged Burners As was pointed out earlier under "Pollutant Formation and Control in Flames," the proper staging of fuel or air in the combustion process is one technique for minimizing NO_x emissions. Gas burners that achieve such staging are available.

Air-Staged Burners Low-NO_x air-staged burners for firing gas (or oil) are shown in Figs. 27-30 and 27-31. A high-performance, low-NO_x burner for high-temperature furnaces is shown in Fig. 27-35. In this design, both air-staging and external flue-gas recirculation are used to achieve extremely low levels of NO_x emissions (approximately 90 percent lower than conventional burners). The flue gas is recirculated by a jet-pump driven by the primary combustion air.

Fuel-Staged Burners Use of fuel-staged burners is the preferred combustion approach for NO_x control because gaseous fuels typically contain little or no fixed nitrogen. Figure 27-36 illustrates a fuel-staged natural draft refinery process heater burner. The fuel is split into primary (30 to 40 percent) and secondary (60 to 70 percent) streams. Furnace gas may be internally recirculated by the primary gas jets for additional NO_x control. NO_x reductions of 80 to 90 percent have been achieved by staging fuel combustion.

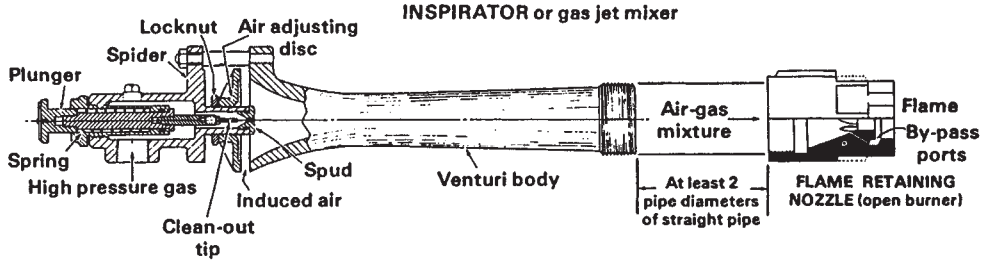


FIG. 27-33 Inspirator (gas-jet) mixer feeding a large port premix nozzle of the flame retention type. High-velocity gas emerging from the spud entrains and mixes with air induced in proportion to the gas flow. The mixture velocity is reduced and pressure is recovered in the venturi section. (*From* North American Combustion Handbook, *3d ed., North American Manufacturing Company, Cleveland, 1996.*)

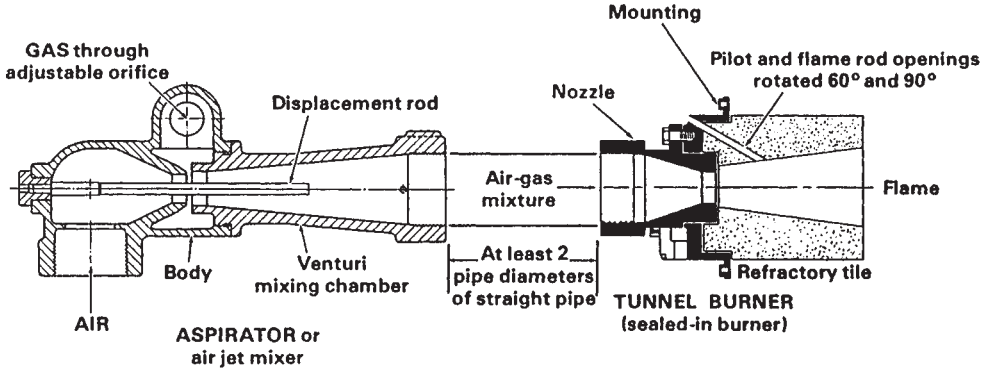


FIG. 27-34 Aspirator (air-jet) mixer feeding a sealed-in large port premix tunnel burner. Blower air enters at lower left. Gas from an atmospheric regulator is pulled into the air stream from the annular space around the venturi throat in proportion to the air flow. (*From* North American Combustion Handbook, *3d ed., North American Manufacturing Company, Cleveland, 1996.*)

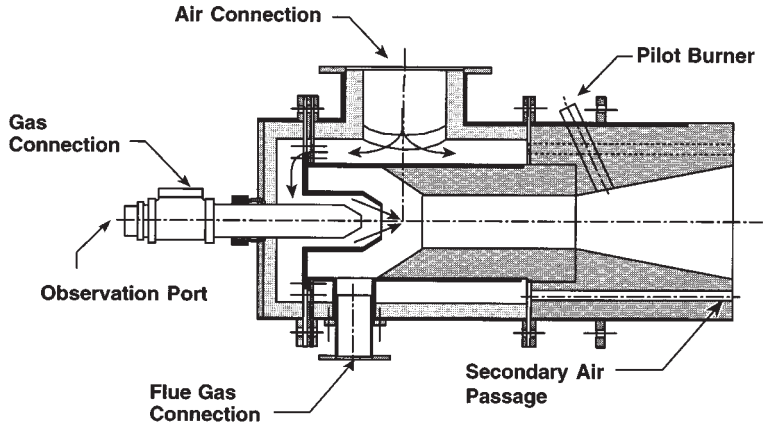


FIG. 27-35 Low-NO_x burner with air-staging and flue-gas recirculation for use in high-temperature furnaces. (*Hauck Manufacturing Company. Developed and patented by the Gas Research Institute.*)

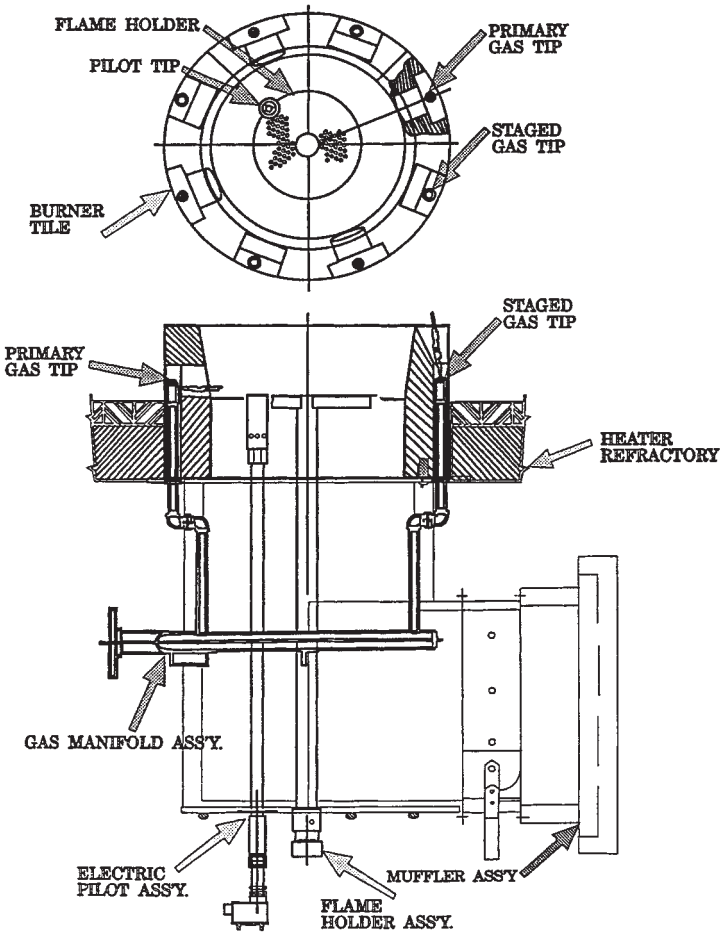


FIG. 27-36 Low-NO_x fuel-staged burner for a natural draft refinery process heater. (*Callidus Technologies, Inc.*)

THERMAL ENERGY CONVERSION AND UTILIZATION

BOILERS

Steam generators are designed to produce steam for process requirements, for process needs along with electric power generation, or solely for electric power generation. In each case, the goal is the most efficient and reliable boiler design for the least cost. Many factors influence the selection of the type of steam generator and its design, and some of these will be treated later in discussions of industrial and utility boilers.

Figure 27-37 shows the chief operating characteristics of a range of boilers, from small-scale heating systems to large-scale utility boilers.

In the industrial market, boilers have been designed to burn a wide range of fuels and operate at pressures up to 12.4 MPa (1800 psia) and steaming rates extending to 455,000 kg/h (1,000,000 lb/h). High-capacity shop-assembled boilers (package boilers) range in capacity from 4545 kg/h (10,000 lb/h) to about 270,000 kg/h (600,000 lb/h). These units are designed for operation at pressures up to 11.4 MPa (1650 psia) and 783 K (950°F). Figure 27-38 shows a gas- or liquid-fuel-fired unit. While most shop-assembled boilers are gas- or oil-fired, designs are available to burn pulverized coal. A field-erected coal-fired industrial boiler is shown in Fig. 27-39.

Boilers designed for service in electric power utility systems operate at both subcritical-pressure (pressures below 22.1 MPa [3205 psia]) and supercritical-pressure steam conditions. Subcritical-pressure boilers range in design pressures up to about 18.6 MPa (2700 psia) and in steaming capacities up to about 2955 Mg/h (6,500,000 lb/h). Supercritical-pressure boilers have been designed to operate at pressures up to 34.5 MPa (5000 psia). The 24.1 MPa (3500 psia) cycle has been firmly established in the utility industry, and boilers with steaming capacities up to 4227 Mg/h (9,300,000 lb/h) and superheat and reheat temperatures of 814 K (1005°F) are in service. The furnace of a large coal-fired steam generator absorbs half of the heat released, so that the gas temperature leaving the furnace is about 1376 K (2000°F).

Boiler Design Issues Boiler design involves the interaction of many variables: water-steam circulation, fuel characteristics, firing systems and heat input, and heat transfer. The furnace enclosure is one of the most critical components of a steam generator and must be conservatively designed to assure high boiler availability. The furnace configuration and its size are determined by combustion requirements, fuel characteristics, emission standards for gaseous effluents and particulate matter, and the need to provide a uniform gas flow and temperature entering the convection zone to minimize ash deposits and excessive superheater metal temperatures. Discussion of some of these factors follows.

Circulation and Heat Transfer Circulation, as applied to a steam generator, is the movement of water or steam or a mixture of both through the heated tubes. The circulation objective is to absorb heat from the tube metal at a rate that assures sufficient cooling of the furnace-wall tubes during all operating conditions, with an adequate margin of reserve for transient upsets. Adequate circulation prevents excessive metal temperatures or temperature differentials that would cause failures due to overstressing, overheating, or corrosion.

The rate of heat transfer from the tubes to the fluid depends primarily on turbulence and the magnitude of the heat flux itself. Turbulence is a function of mass velocity of the fluid and tube roughness. Turbulence has been achieved by designing for high mass velocities, which ensure that nucleate boiling takes place at the inside surface of the tube. If sufficient turbulence is not provided, *departure from nucleate boiling* (DNB) occurs. DNB is the production of a film of steam on the tube surface that impedes heat transfer and results in tube overheating and possible failure. This phenomenon is illustrated in Fig. 27-40.

Satisfactory performance is obtained with tubes having helical ribs on the inside surface, which generate a swirling flow. The resulting centrifugal action forces the water droplets toward the inner tube surface and prevents the formation of a steam film. The internally rifled tube maintains nucleate boiling at much higher steam temperature and pressure and with much lower mass velocities than those needed in smooth tubes. In modern practice, the most important criterion in drum boilers is the prevention of conditions that lead to DNB.

Utility Steam Generators

Steam-Generator Circulation System Circulation systems for utility application are generally classified as natural circulation and forced or pump-assisted circulation in drum-type boilers, and as once-through flow in subcritical- and supercritical-pressure boilers. The

Boiler Service	Fuel	Capacity (kg/h)	Outlet Pressure (MPa)	Steam Temp. (K)	Reheat Temp. (K)	Feedwater Temp. (K)
Heating	Oil	27,000	1.0	Sat	-	373
Small Industrial	Oil	45,000	4.6	673	-	423
Medium Industrial	Coal	115,000	4.6	673	-	403
Large Industrial	Coal	270,000	10.4	745	-	408
Large Utility	Coal	1,700,000	18.2	811	811	522

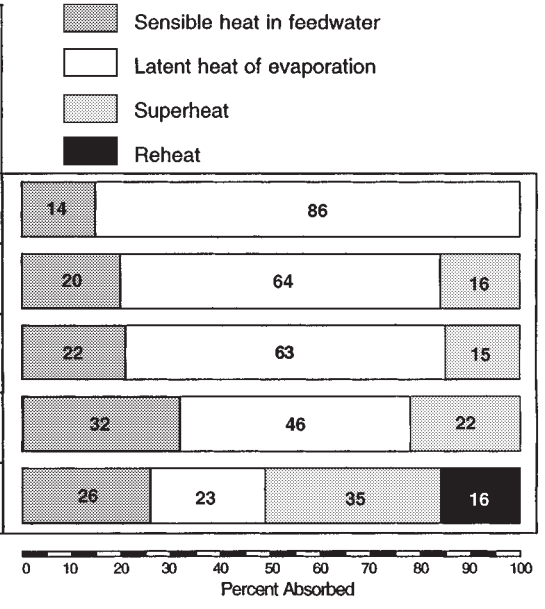


FIG. 27-37 Heat absorption distribution for various types of boilers. (*Adapted from Singer,* Combustion—Fossil Power, *4th ed., Combustion Engineering, Inc., Windsor, Conn., 1991.*)

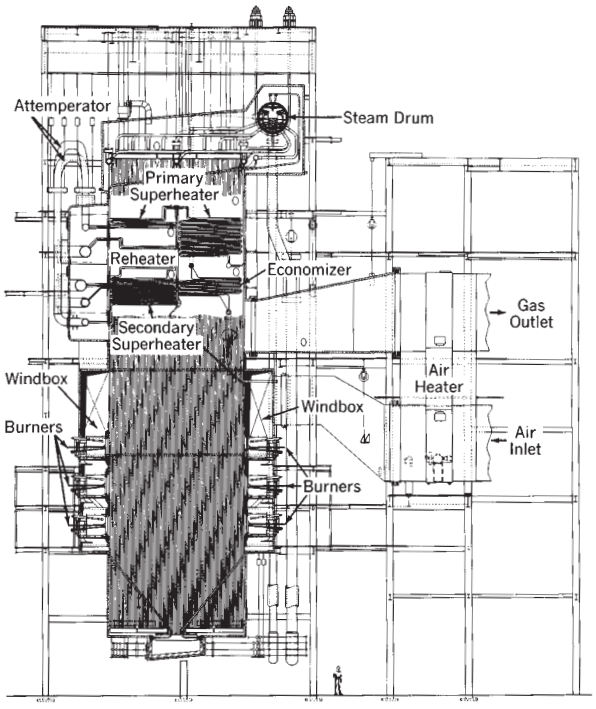


FIG. 27-38 Shop-assembled radiant boiler for natural gas or oil. (*Babcock & Wilcox Co.*)

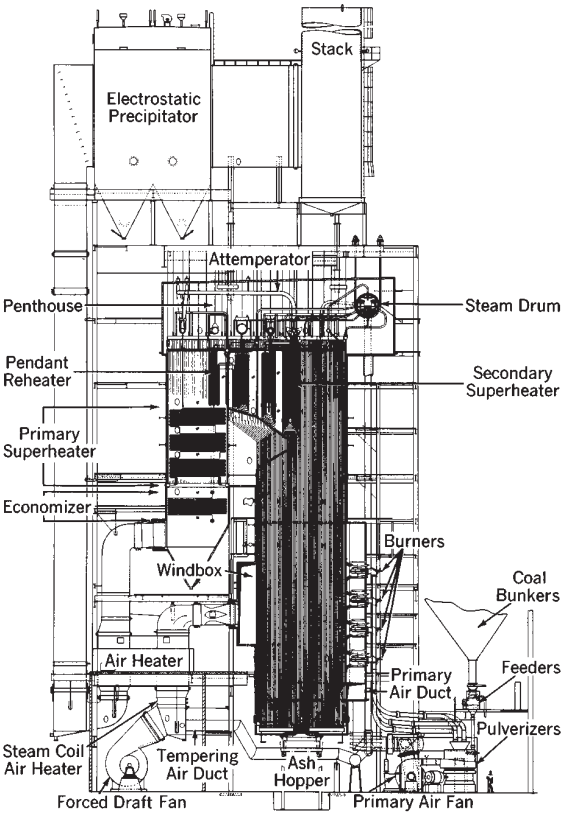


FIG. 27-39 Field-erected radiant boiler for pulverized coal. (*Babcock & Wilcox Co.*)

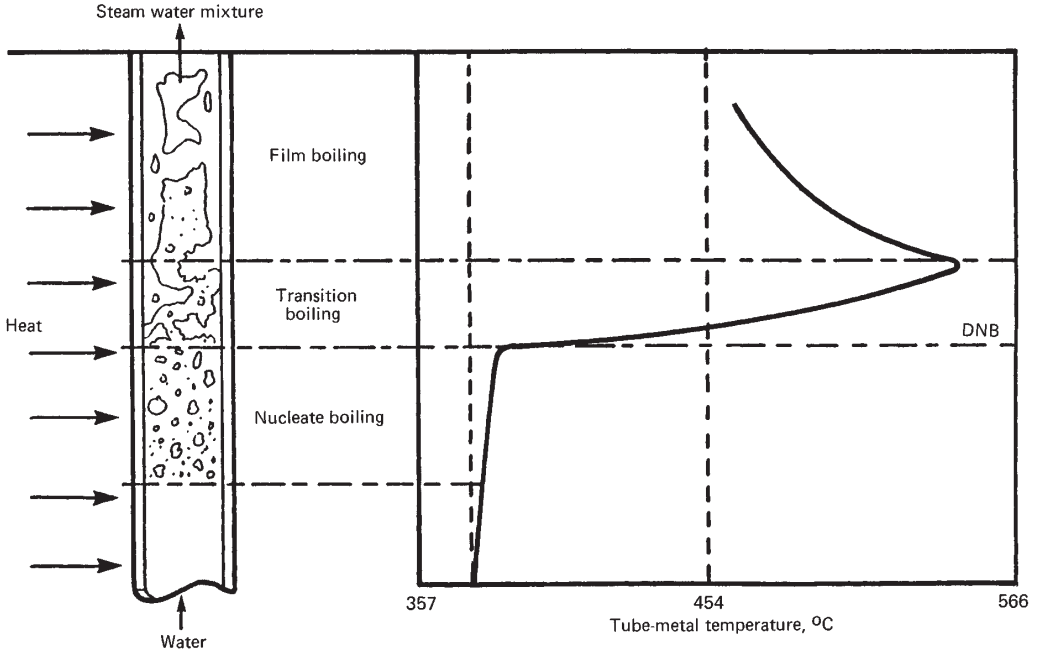


FIG. 27-40 Effect of departure from nucleate boiling (DNB) on tube-metal temperature.

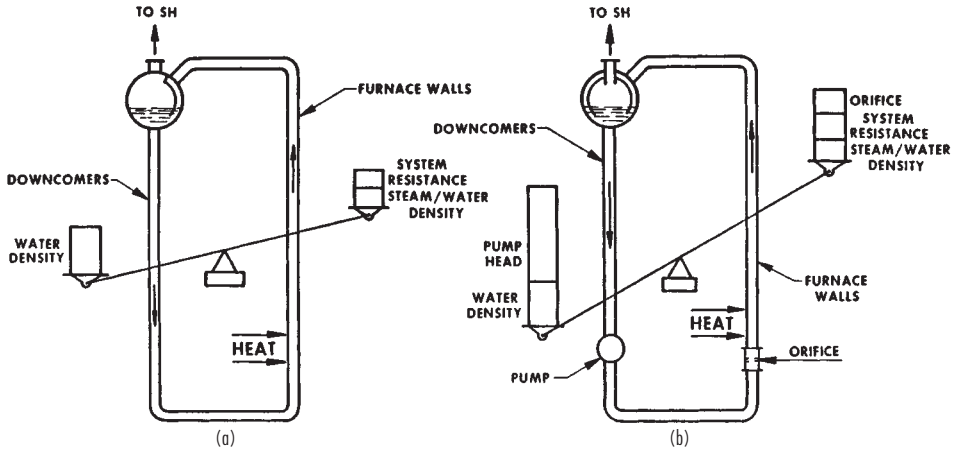


FIG. 27-41 Circulation systems: (*a*) natural circulation; (*b*) pump-assisted circulation.

circulation systems for natural and pump-assisted circulation boilers are illustrated schematically in Fig. 27-41.

Natural circulation in a boiler circulation loop depends only on the difference between the mean density of the fluid (water) in the downcomers and the mean density of the fluid (steam-water mixture) in the heated furnace walls. The actual circulating head is the difference between the total gravity head in the downcomer and the integrated gravity heads in the upcoming legs of the loop containing the heated tubes. The circulating head must balance the sum of the losses due to friction, shock, and acceleration throughout the loop.

In a once-through system, the feedwater entering the unit absorbs heat until it is completely converted to steam. The total mass flow through the waterwall tubes equals the feedwater flow and, during normal operation, the total steam flow. As only steam leaves the boiler, there is no need for a steam drum.

Fuel Characteristics Fuel choice has a major impact on boiler design and sizing. Because of the heat transfer resistance offered by ash deposits in the furnace chamber in a coal-fired boiler, the mean absorbed heat flux is lower than in gas- or oil-fired boilers, so a greater surface area must be provided. Figure 27-42 shows a size comparison between a coal-fired and an oil-fired boiler for the same duty.

In addition, coal characteristics have a major impact on the design and operation of a coal-fired boiler. Coals having a low volatile-matter content usually require higher ignition temperatures and those with less than 12 to 14 percent volatile matter may require supplementary fuel to stabilize ignition. Generally, western U.S. coals are more reactive than others and, consequently, easier to ignite, but because of high moisture content they require higher air temperatures to the mills for drying the coal to achieve proper pulverization. Extremely high-ash coal also may present problems in ignition and stabilization. The ash constituents and the quantity of ash will have a decided influence on sizing the furnace. Accordingly, a thorough review of coal characteristics is needed to establish the effect on the design and operation of a boiler.

Superheaters and Reheaters A superheater raises the temperature of the steam generated above the saturation level. An important function is to minimize moisture in the last stages of a turbine to avoid blade erosion. With continued increase of evaporation temperatures and pressures, however, a point is reached at which the available superheat temperature is insufficient to prevent excessive moisture from forming in the low-pressure turbine stages. This condition is resolved by removing the vapor for reheat at constant pressure in the

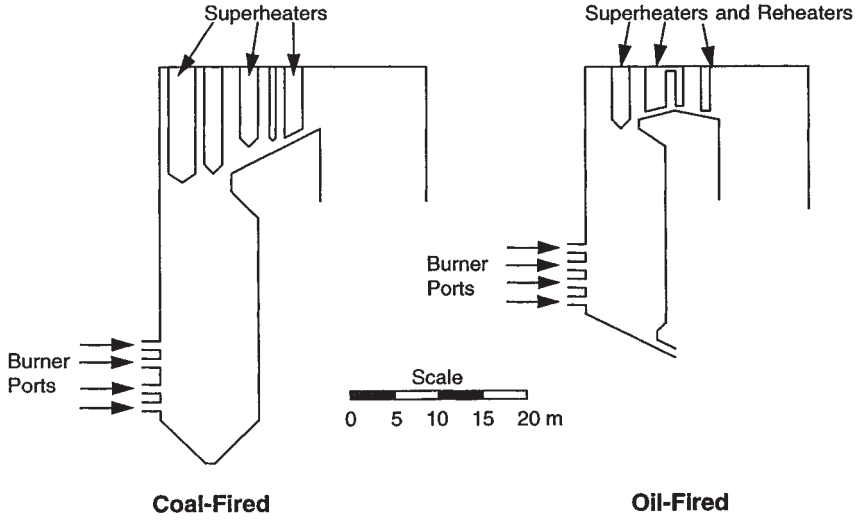


FIG. 27-42 Comparison of the sizes and shapes of typical 500-MW_e coal- and oil-fired boilers. (*Adapted with permission from Lawn,* Principles of Combustion Engineering for Boilers, *Academic Press, London, 1987.*)

boiler and returning it to the turbine for continued expansion to condenser pressure. The thermodynamic cycle using this modification of the Rankine cycle is called the *reheat cycle.*

Economizers Economizers improve boiler efficiency by extracting heat from the discharged flue gases and transferring it to feedwater, which enters the steam generator at a temperature appreciably lower than the saturation-steam temperature.

Industrial Boilers Industrial boilers are steam generators that provide power, steam, or both to an industrial plant, in contrast to a utility boiler in a steam power plant. A common configuration is a stationary water-tube boiler in which some of the steam is generated in a convection-section tube bank (also termed a *boiler bank*). In the original industrial boilers, in fact, almost all of the boiling occurred in that section, but now many industrial steam generators of 180,000 kg/h (397,000 lb/h) and greater capacity are radiant boilers. The boiler steam pressure and temperature and feedwater temperature determine the fraction of total heat absorbed in the boiler bank. For a typical coal-fired boiler producing about 90,000 kg/h (198,000 lb/h):

%, total steam in boiler bank	Boiler pressure		Steam temperature		Feedwater temperature	
	MPa	psia	K	°F	K	°F
45	1.4	200	460	369	389	241
30	4.1	600	672	750	389	241
16	10.3	1500	783	950	450	351
10	12.4	1800	811	1000	450	351

The thicker plate for operation at higher pressures increases the cost of the boiler. As a result, it is normally not economical to use a boiler bank for heat absorption at pressures above 10.7 MPa (1550 psia).

Industrial boilers are employed over a wide range of applications, from large power-generating units with sophisticated control systems, which maximize efficiency, to small low-pressure units for space or process heating, which emphasize simplicity and low capital cost. Although their usual primary function is to provide energy in the form of steam, in some applications steam generation is incidental to a process objective, e.g., a chemical recovery unit in the paper industry, a carbon monoxide boiler in an oil refinery, or a gas-cooling waste-heat boiler in an open-hearth furnace. It is not unusual for an industrial boiler to serve a multiplicity of functions. For example, in a paper-pulp mill, the chemical-recovery boiler is used to convert black liquor into useful chemicals and to generate process steam. At the same plant, a bark-burning unit recovers heat from otherwise wasted material and also generates power.

Industrial boilers burn oil, gas, coal, and a wide range of product and/or waste fuels, some of which are shown in Tables 27-4 and 27-19. Natural gas has become the principal fuel of choice, accounting for approximately two-thirds of all the energy fired in industrial boilers across a wide range of manufacturing industries (Table 27-20). Coal is the second most prevalent fuel, accounting for one-quarter of the energy fired. Waste fuels, however, are increasing in importance.

An excellent brief exposition of industrial boilers is presented as Chapter 8 of *Combustion—Fossil Power,* Singer (ed.), 4th ed., Combustion Engineering, Windsor, Conn., 1991.

Design Criteria Industrial-boiler designs are tailored to the fuels and firing systems involved. Some of the more important design criteria include:

- Furnace heat-release rates, both W/m^3 and W/m^2 of effective projected radiant surface (Btu/[h·ft^3] and Btu/[h·ft^2]).
- Heat release on grates
- Flue-gas velocities through tube banks
- Tube spacings

Table 27-21 gives typical values or ranges of these criteria for gas, oil, and coal. The furnace release rates are important, for they establish maximum local absorption rates within safe limits. They also have a bearing on completeness of combustion and therefore on efficiency and particulate emissions. Limiting heat release on grates (in stoker firing) will minimize carbon loss, control smoke, and avoid excessive fly ash.

Limits on flue-gas velocities for gas- or oil-fired industrial boilers

TABLE 27-19 Solid-Waste Fuels Burned in Industrial Boilers

Waste	HHV, kJ/kg*
Bagasse	8374–11,630
Furfural residue	11,630–13,956
Bark	9304–11,630
General wood wastes	10,467–18,608
Coffee grounds	11,397–15,119
Nut hulls	16,282–18,608
Rich hulls	12,095–15,119
Corncobs	18,608–19,306
Rubber scrap	26,749–45,822
Leather	27,912–45,822
Cork scrap	27,912–30,238
Paraffin	39,077
Cellophane plastics	27,912
Polyvinyl chloride	40,705
Vinyl scrap	40,705
Sludges	4652–27,912
Paper wastes	13,695–18,608

*To convert kilojoules per kilogram to British thermal units per pound, multiply by 4.299×10^{-1}.

TABLE 27-20 Fuel Consumption in Boilers in Various Industries

Industry	Annual energy consumption in boilers, PJ/a*			
	Residual oil	Distillate oil	Natural gas	Coal
Aluminum	—	—	2	—
Steel	25	—	66	25
Chemicals	29	6	759	257
Forest products	140	4	381	309
Textiles	12	5	74	32
Fabricated metal	2	1	39	5
Industrial machinery & equipment	3	4	115	12
Transportation equipment	—	2	51	—
Food	25	7	332	151
Petroleum refining	35	2	267	3
TOTAL	27	31	2086	794

SOURCE: *Manufacturing Consumption of Energy,* Energy Information Administration, U.S. Dept. Energy, 1991.

*Within the limit of their probable accuracy, the values of this table are acceptable also for the units of 10^{12} Btu/a. For accurate *conversion,* however, they must be reduced by 5.2 percent.

TABLE 27-21 Typical Design Parameters for Industrial Boilers

Furnace	Heat-release rate, W/m^2* of EPRS†
Natural gas-fired	630,800
Oil-fired	551,900–630,800
Coal: pulverized coal	220,780–378,480
Spreader stoker	252,320–410,020

Stoker, coal-fired	Grate heat-release rate, W/m^2
Continuous-discharge spreader	2,050,000–2,207,800
Dump-grade spreader	1,419,300–1,734,700
Overfeed traveling grate	1,261,000–1,734,700

Flue-gas velocity: type Fuel-fired	Single-pass	Baffled	
	Boiler, m/s	Boiler, m/s	Economizer, m/s
Gas or distillate oil	30.5	30.5	30.5
Residual oil	30.5	22.9	30.5
Coal (not lignite)			
Low-ash	19.8–21.3	15.2	15.2–18.3
High-ash	15.2	NA‡	12.2–15.2

*To convert watts per square meter to British thermal units per hour-foot, multiply by 0.317.

†Effective projected radiant surface.

‡Not available.

are usually determined by the need to limit draft loss. For coal firing, design gas velocities are established to minimize fouling and plugging of tube banks in high-temperature zones and erosion in low-temperature zones.

Convection tube spacing is important when the fuel is residual oil or coal, especially coal with low ash-fusion or high ash-fouling tendencies. The amount of the ash and, even more important, the characteristics of the ash must be specified for design.

Natural-circulation and convection boiler banks are the basic design features on which a line of standard industrial boilers has been developed to accommodate the diverse steam, water, and fuel requirements of the industrial market.

Figure 27-43 shows the amount of energy available for power by using a fire-tube boiler, an industrial boiler, and subcritical- and supercritical-pressure boilers. Condensing losses decrease substantially, and regeneration of air and feedwater becomes increasingly important in the most advanced central-station boilers.

The boiler designer must proportion heat-absorbing and heat-recovery surfaces in a way to make the best use of heat released by the fuel. Water walls, superheaters, and reheaters are exposed to convection and radiant heat, whereas convection heat transfer predominates in air preheaters and economizers. The relative amounts of these surfaces vary with the size and operating conditions of the boiler.

Package Boilers In a fire-tube boiler, the hot combustion products flow through tubes immersed in the boiler water, transferring heat to it. In a water-tube boiler, combustion heat is transferred to water flowing through tubes which line the furnace walls and boiler passages. The greater safety of water-tube boilers has long been recognized, and they have generally superseded fire-tube configurations except for small package boiler designs. Fire-tube package boilers range from a few hundred to 18,200 kg/h (40,000 lb/h) steaming capacity. A fire-tube boiler is illustrated in Figs. 27-44 and 27-45. Water-tube package boilers range from a few hundred to 270,000 kg/h (600,000 lb/h) steaming capacity. A water-tube package boiler is illustrated in Fig. 27-46. The majority of water-tube package boilers use natural circulation and are designed for pressurized firing. The most significant advantage of shop-assembled or package boilers is the cost benefit associated with use of standard designs and parts.

Package boilers can be shipped complete with fuel-burning equipment, controls, and boiler trim. It may be necessary to ship the larger units in sections, however, and a shop-assembled boiler with a capacity greater than about 109,000 kg/h (240,000 lb/h) is deliverable only by barge. (For a more detailed discussion of shop-assembled boilers, see Singer, 1991, pp. 8.36–8.42.)

Fluidized-Bed Boilers As explained in the earlier discussion of coal combustion equipment, the furnace of a fluid-bed boiler has a unique design. The system as a whole, however, consists mainly of standard equipment items, adapted to suit process requirements. The

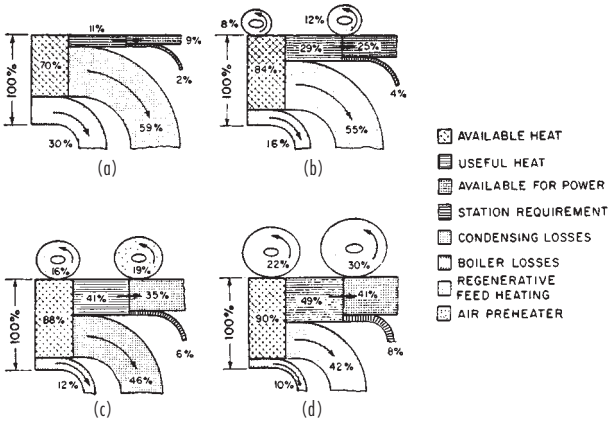


FIG. 27-43 Sankey diagrams for various types of boilers: (*a*) fire-tube boiler; (*b*) industrial boiler; (*c*) subcritical-pressure boiler; (*d*) supercritical-pressure boiler.

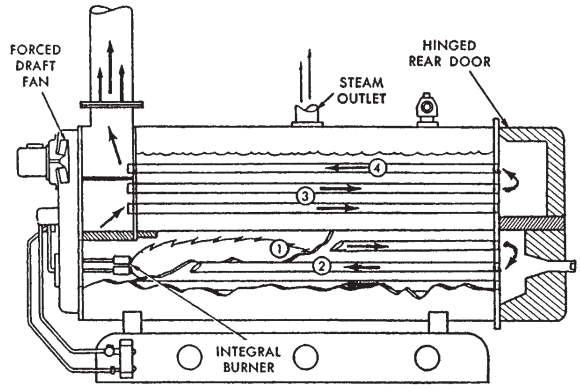


FIG. 27-44 A four-pass packaged fire-tube boiler. Circled numbers indicate passes. (*From Cleaver Brooks, Inc. Reproduced from* Gas Engineer's Handbook, *Industrial Press, New York, 1965, with permission.*)

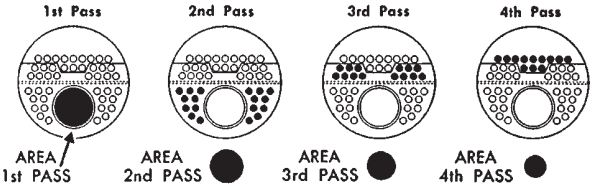


FIG. 27-45 Location and relative size of each of four passes of the flue gas through a fire-tube boiler. (*From Cleaver Brooks, Inc. Reproduced from* Gas Engineer's Handbook, *Industrial Press, New York, 1965, with permission.*)

systems for coal and sorbent preparation and feeding, ash removal, and ash disposal are very similar to those found in PC boiler plants, the major difference being that the top size of material used is greater. The water-wall boiler enclosure and convection-pass tubing are also similar to the designs found in PC boilers. In-bed heat-transfer surfaces are arranged similarly to convection-pass tube banks, but the bubbling action subjects them to higher forces and special consideration has to be given to the design of a suitable support structure. A fluidized-bed plant includes particulate removal equipment such as cyclones, multiclones, baghouses, and electrostatic precipitators, all similar to designs found in other solids-handling process plants.

Bubbling AFBCs A simplified schematic of a bubbling AFBC is presented in Fig. 27-47. A demonstration plant generating 160 MWe, with a power production intensity* of 1.49 MWe/m^2 (1 MWe/16 ft^2), began operation in 1988. Also operating is a 350-MWe unit that employs many of the same design features.

Although subbituminous coal with a top size of 25 mm (1 in) can be fed overbed with good thermal and environmental performance, less reactive bituminous coal must be fed underbed. This requires that the coal be dried and crushed to a top size of 3 mm (⅛ in). A lock-hopper feeder operating at about 0.15 MPa (21 psia) is required to overcome the combined pressure drop across the bed and along the conveying line. A separate lock-hopper system is required to feed the sorbent, also with a top size of 3 mm (⅛ in), but it is introduced into the boiler through the same conveying line. The mixture enters the bed through T nozzles, one per 2 m^2 (22 ft^2) of bed floor area, that divide the flow and distribute it horizontally beneath the tube bank. There is approximately 0.45 m (18 in) between the distributor plate and the bottom of the in-bed tube bank to prevent tube damage by jet impingement from the air and solids feed streams, and to allow access for maintenance. The height of the tube bank itself is around 0.45 m, requiring a normal bed depth of 0.9 m (36 in) to immerse all the tubes completely.

* Power production intensity is the power produced by the boiler per unit area of the plan section of the bed at a stated elevation.

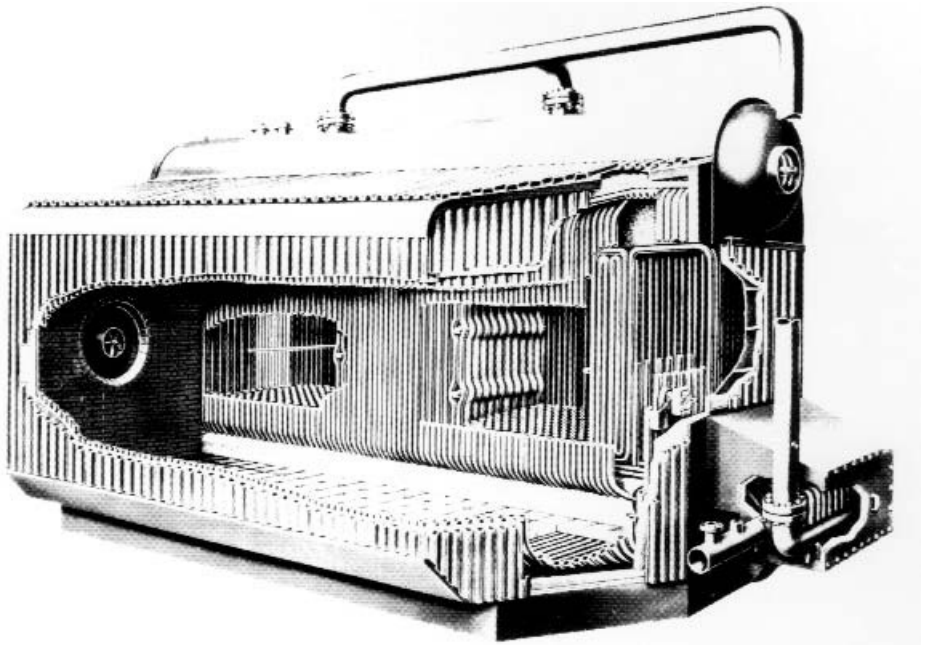


FIG. 27-46 A D-type shop-assembled water-tube boiler. (*Combustion Engineering, Inc.*)

The convection pass cools the flue gas and entrained particulate matter from about 1145 K (1600°F) to below 645 K (700°F). For bituminous coal with a combustion temperature of 1115 K (1550°F), a recycle ratio of 2.5 (mass rate of particulate recycle to coal feed rate) increases combustion efficiency to over 97 percent from around 90 percent without recycle. For a bituminous coal containing 3 percent sulfur, 90 percent sulfur capture is achieved with limestone as sorbent at a calcium-to-sulfur (Ca/S) molar ratio of 2.3 and a recycle ratio of 2.5. A Ca/S molar ratio of over 3.4 is required when there is no recycle. The recycled material also enters the bed through T nozzles, one per 7 m^2 (72 ft^2) of bed floor area. A means of distributing the particulate flow from the multiclones to the feed lines and overcoming the back pressure is required. On the 160-MWe unit, the back pressure is overcome by means of a J-valve.

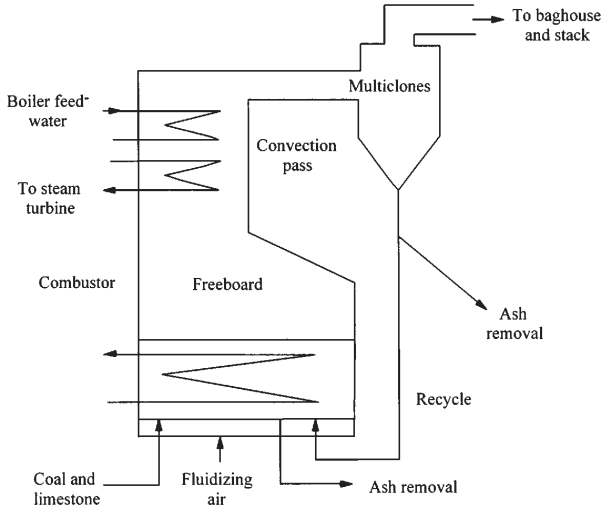


FIG. 27-47 Simplified flow diagram for bubbling AFBC (with underbed feed system).

A typical NO_x level in the combustion gas is around 107 mg/MJ (0.25 lb/10^6 Btu), and the CO level tends to be high (near 86 mg/MJ [0.20 lb/10^6 Btu]). Only one design has used secondary air, and this lowered the NO_x to 86 mg/MJ and the CO to about 43 mg/MJ (0.10 lb/10^6 Btu). NO_x reduction by selective noncatalytic reduction (SNCR) has not been tested in a bubbling AFBC, but without the assistance of secondary air, it may be difficult to distribute the ammonia adequately across the freeboard to achieve the desired effect.

Approximately 85 percent of the heat is released in the bed and the other 15 percent above the bed. Typical heat flux data are tabulated in Table 27-22 for a mean bed temperature of 1115 K (1550°F).

The in-bed heat transfer rate decreases with mean bed particle size. As there is no accurate means of predicting this particle size, even if that of the feedstocks is known, there is a design uncertainty vis-à-vis heat transfer coefficient. If heat exchanger area adjustment has to be made after the boiler is in operation, surface is removed more easily than added. A reasonable design strategy, therefore, is to use an overall coefficient from the lower portion of the range experienced in practice. Then, if the actual coefficient is found to be higher than the design value, the bed temperature needed to maintain the design steam rate will be lower than specified. If the lower bed temperature adversely affects process performance and boiler efficiency, then surface area may need to be removed.

TABLE 27-22 Heat Absorption Distribution in Bubbling AFBCs

	Heat absorption split, %	Heat flux, kW/m^2 (Btu/h·ft^2)
In-bed tubing		
Evaporators	25	147 (46,500)
Superheaters	15	112 (35,500)
Walls	5	134 (42,500)
Freeboard water walls	10	44 (14,000)
Convection pass		
Superheater	20	15 (4,750)
Reheater	15	22 (6,850)
Economizer	10	6.5 (2,050)

Mean bed particle size (thus, the in-bed heat-transfer coefficient) may vary for external reasons such as a change of feedstock supply or a deterioration in crusher performance. This potential source of variation should be considered before any decision to resurface is made.

Circulating AFBCs The circulating AFBC is now more widely used than the bubbling version. A simplified schematic for a design with an external heat exchanger is presented in Fig. 27-48. A 110-MWe demonstration plant had a power production intensity of 1 MWe/m^2 (1 MWe/11 ft^2), almost 50 percent greater than that of a comparable bubbling unit. Circulating AFBC units of 250 MWe are now in service and larger units are being planned.

Circulating AFBCs handle bituminous and subbituminous coals equally well, and their coal preparation and feeding systems are far simpler than those of bubbling versions. The coal is crushed to a top size of 12 mm (½ in), without drying, and fed by gravity into the lower refractory-lined portion of the boiler. The feed points are close to the pressure balance point and so there is little, if any, back pressure; this greatly reduces the sealing requirements. In addition, and sometimes alternatively, the coal can be introduced into the cyclone ash return lines. A minimum of four coal entry points is required to achieve uniform feed distribution in the 110-MWe unit, corresponding to one per 30 m^2 (300 ft^2) of freeboard cross section. High turbulence and the absence of in-bed tubing facilitate adequate mixing of the coal across the combustor. The sorbent is prepared to a top size of 1 mm (0.04 in) and dried so that it can be pneumatically fed to the combustor. Experience showed that no less than eight sorbent feed points were required on the 110-MWe unit (one per 15 m^2 [150 ft^2] of freeboard cross section) to achieve satisfactory performance. Load control is achieved primarily by reducing coal feed rate, with a corresponding reduction in air flow, to lower combustor temperature.

Almost all of the particulate matter leaving the boiler is collected by cyclones and recycled to the base of the unit. The number of cyclones varies in different design concepts, but each cyclone can serve 40 to 60 MWe of generating capacity (in the case of the 110-MWe unit, one recycle point per 60 m^2 (600 ft^2) of freeboard cross section). The collected particulate matter is returned against a backpressure of 0.02 MPa (3 psi), through a J-valve. The recycle ratio can be as high as 40:1, corresponding to a relatively long mean particle residence time and accounting for the high performance of circulating units. For a bituminous coal containing 3 percent sulfur, with limestone sorbent and a combustion temperature of 1115 K (1550°F), the combustion efficiency is 99.0 percent, and 90 percent sulfur retention is attained with a Ca/S molar ratio of 2.2. The NO_x value at this temperature is typically 86 mg/MJ (0.20 lb/MBtu), but it can be reduced to below 43 mg/MJ (0.1 lb/MBtu) by ammonia injected with the secondary air. The corresponding CO level is about 43 mg/MJ.

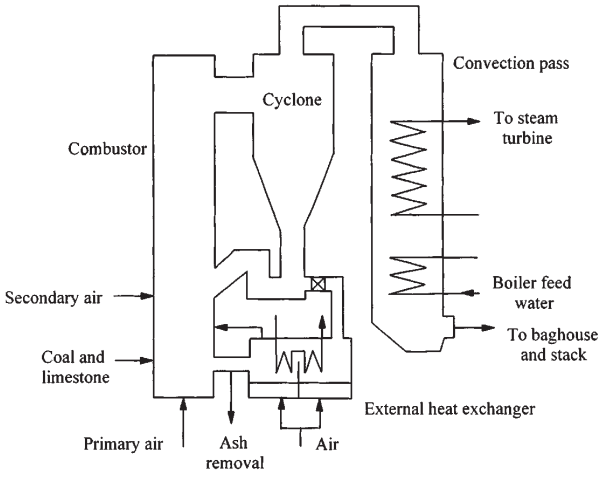


FIG. 27-48 Simplified flow diagram for circulating AFBC (with external heat exchanger).

Bubbling PFBCs Like the AFBC, the bubbling PFBC offers the ability to achieve low SO_2 and NO_x emissions without back-end add-on control equipment. It also offers advantages that the AFBC does not. Pressurized operation results in the boiler being more compact with a reduction in capital cost. Expanding the pressurized flue gas through a gas turbine generator, in combination with a steam turbine generator, increases cycle efficiency and increases power output by up to 25 percent. The lower capital cost and higher efficiency result in a lower cost of electricity.

A PFBC boiler is visually similar to an AFBC boiler. The combustor is made of water-wall tubing, which contains the high-temperature environment, but the whole assembly is placed within a pressure vessel. Unlike an AFBC unit, there is no convection pass, as the flue-gas temperature must be maintained at boiler temperature to maximize energy recovery by the expansion turbine. There is an economizer after the turbine for final heat recovery. A simplified schematic is presented in Fig. 27-49. An 80-MWe demonstration plant, operating at 1.2 MPa (180 psia), began operation in 1989 with a power production intensity of 3 MWe/m^2 (1 MWe/3.5 ft^2). By 1996, five units of this size had been constructed, and a 320-MWe unit is planned to commence operation in 1998.

The boiler, primary and secondary flue-gas cyclones, and ash-cooling circuits are installed within a pressure vessel operating at up to 1.7 MPa (240 psia). Also enclosed are the vessels that store bed material at operating temperature. These facilitate load control by allowing bed level to be raised or lowered rapidly, thus covering or exposing in-bed heat transfer surface and regulating both steam production and gas turbine inlet temperature. Reduced bed level and flue-gas temperature at part load result in some reduction in combustion performance. After leaving the cyclones, which remove over 99 percent of the particulate matter, the flue gas passes down the center of a coaxial pipe to the gas turbine. A custom-designed variable-speed gas turbine is used that is tolerant to the low levels of fine residual particulate matter. The compressed air is delivered to the pressure vessel through the annular portion of the coaxial pipe. This eliminates the need for a refractory-lined pipe and precludes the possibility of refractory passing to the gas turbine and damaging it. A baghouse is used for final particulate matter removal before discharging the flue gas to atmosphere.

Coal is fed as a paste containing 25 wt % water, and sorbent is fed dry by a lock-hopper system with pneumatic conveying. The top size of each feedstock is 3 mm (⅛ in). The latent heat lost evaporating the water fed with the paste is compensated by increased gas turbine power output resulting from the increased flue-gas mass flow rate. For the 80-MWe unit, there are six coal feed points (one per 4.5 m^2 [48 ft^2]) and four sorbent feed points (one per 6.7 m^2 [72 ft^2]), all entering beneath the tube bank along one wall. The bed depth is

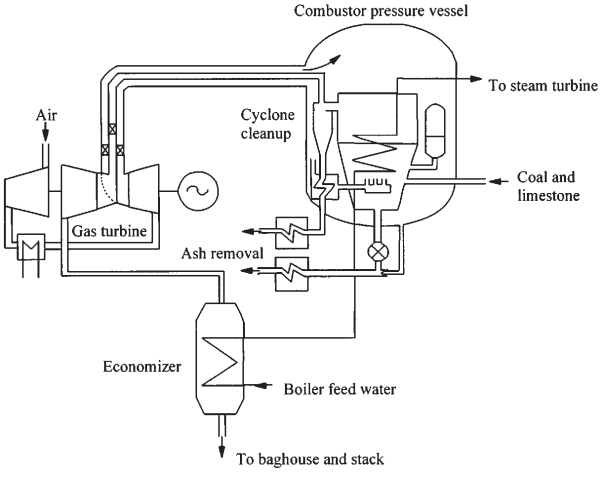


FIG. 27-49 Simplified flow diagram for bubbling PFBC.

about 3.7 m (12 ft) and the tube bank is about 3 m (10 ft) tall. The deep bed increases the in-bed gas residence time to around 4 s compared to less than 0.5 s in a bubbling AFBC unit. For bituminous coal containing 3 percent sulfur, with limestone sorbent and a combustion temperature of 1115 K (1550°F), this residence time allows combustion efficiencies in excess of 99 percent to be achieved without recycle, and 90 percent sulfur capture with a Ca/S molar ratio of 1.9. NO_x values of about 107 mg/MJ (0.25 lb/10^6 Btu) can be reduced to 21 mg/MJ (0.05 lb/10^6 Btu) by SNCR. Although the inherent NO_x level is similar to that achieved in bubbling AFBC units, the CO levels are very much lower, 13 mg/MJ (0.03 lb/10^6 Btu) being attainable.

Over 98 percent of the heat is released in the bed. For similar mean bed temperatures and mean bed particle sizes, the elevated operating pressure results in heat fluxes to the in-bed tubing that are typically 15 to 20 percent greater than in a bubbling AFBC unit.

Circulating PFBC Circulating PFBC technology has been under development only since the late 1980s and is still in the pilot-plant stage. A simplified schematic for a design without an external heat exchanger is presented in Fig. 27-50. An 80-MWe demonstration plant is planned as part of the U.S. Department of Energy Clean Coal Technology Program; operation is likely in 1999.

Compared to bubbling PFBCs, these boilers operate at similar pressures but at higher fluidizing velocities. As a result, the design is more compact, with a projected power production intensity of 10 MWe/m^2 (1 MWe/ft^2), over three times that of the bubbling design. Being more compact implies a pressure vessel of smaller diameter and a plant design adaptable to more modular construction and more shop assembly, with corresponding lower capital cost. Because the boiler is smaller, better distribution of coal and sorbent can be achieved with fewer feed nozzles. Inasmuch as there is no bed level to be maintained, a finer sorbent can be used, allowing it to be more fully utilized. Load control is achieved by cutting back on the air flow while keeping the combustion temperature substantially constant. This maintains high combustion and sulfur-retention performance over the load range and eliminates the need for bed storage vessels. Fewer cyclones are required (one per 80 MWe) and, as the ash collected is recycled, there are no ash coolers. The design uses high-temperature, high-pressure (HTHP) filtration to clean the flue gas prior to its entering the gas turbine. This virtually particulate-free gas allows conventional gas turbines to be used, increasing the selection available, and at the same time eliminates the need for a back-end baghouse.

For a bituminous coal containing 3 percent sulfur with limestone sorbent and a combustion temperature of 1115 K (1550°F), combustion efficiency in excess of 99 percent can be achieved, as can 90 percent sulfur capture with a Ca/S molar ratio of 1.15. The reduced sorbent demand decreases the amount of ash discharged. NO_x values are around 86 mg/MJ (0.20 lb/10^6 Btu) and can be reduced to 21 mg/MJ (0.05 lb/10^6 Btu) by SNCR reactions. As in the case of the bubbling PFBC, the inherent NO_x level is similar to that achieved in circulating AFBC units, but the CO level is very much lower, 13 mg/MJ (0.03 lb/10^6 Btu) being achieved. No heat flux data to the walls are available at present.

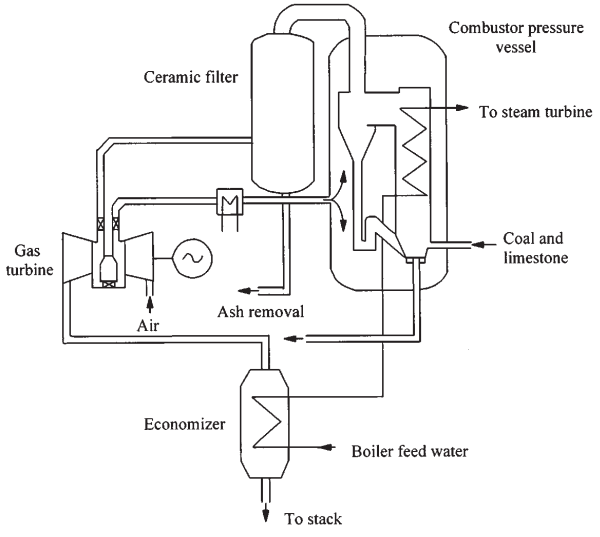


FIG. 27-50 Simplified flow diagram for circulating PFBC.

If all these process and economic advantages are realized, the cost of electricity will be lowered, making circulating PFBC an extremely attractive coal-fired option for power generation.

Advanced PFBC Cycle The latest development in fluidized-bed combustion technology is the concept of an advanced PFBC that generates a fuel gas to feed a high-temperature gas turbine. The efficiency of current combined-cycle plants employing state-of-the-art bubbling or circulating PFBC boilers is limited to about 42 percent (HHV basis) because the maximum permissible combustion gas temperature (therefore, inlet temperature for the gas turbine) is 1145 K (1600°F). At higher bed temperature, the combustor feedstocks can release alkali metal vapor that can lead to fouling and corrosion of the gas turbine blades. Furthermore, the threat of bed ash agglomeration is increased.

The proposed advanced PFBC cycle will permit a turbine inlet gas temperature of over 1535 K (2300°F) by burning a fuel gas produced by pyrolysis of the coal feed. Because the turbine fuel gas must be practically particulate free, it passes through HTHP filters before combustion. The char residue from the pyrolyzer may be burned in a circulating AFBC or PFBC to produce steam for power or heating. The efficiency attainable in an advanced PFBC plant may be as high as 50 percent (HHV basis).

This technology is still in the early pilot stages, the first tests having been conducted in the early 1990s; therefore, insufficient data are available for meaningful comparison with the other PFBC technologies. Nevertheless, it is considered to be potentially the most economic PFBC technology, and development work is continuing with the objective of designing a demonstration plant.

The capital investment for any FBC plant depends upon several factors, including the cost of capital, size of unit, geographic location, and coal type. EPRI has completed several economic evaluations and projects the following costs, in 1994 US dollars, for plants located in Kenosha, Wisconsin, burning Illinois No. 6 bituminous coal containing 4 percent sulfur: 200-MWe circulating AFBC, $1520/kW; 350-MWe bubbling PFBC, $1220/kW; 350-MWe circulating PFBC, $1040/kW; 320-MWe advanced PFBC, $1110/kW. The advanced PFBC has the most potential for cost reduction, and capital investment could be reduced to below $1000/kW.

PROCESS HEATING EQUIPMENT

Many major energy-intensive industries depend on direct-fired or indirect-fired equipment for drying, heating, calcining, melting, or chemical processing. This subsection discusses both direct- and indirect-fired equipment, with the greater emphasis on indirect firing for the process industries.

Direct-Fired Equipment Direct-fired combustion equipment transfers heat by bringing the flame and/or the products of combustion into direct contact with the process stream. Common examples are rotary kilns, open-hearth furnaces, and submerged-combustion evaporators. Table 27-23 gives the average energy consumption rates for various industries and processes that use direct heat. Section 11 of this handbook describes and illustrates rotary dryers, rotary kilns, and hearth furnaces. Forging, heat treating, and metal milling furnaces are discussed by Mawhinney (*Marks' Standard Handbook for Mechanical Engineers,* 9th ed., McGraw-Hill, New York, 1987, pp. 7.47–7.52). Other direct-fired furnaces are described later in this section.

Indirect-Fired Equipment (Fired Heaters) Indirect-fired combustion equipment (fired heaters) transfers heat across either a metallic or refractory wall separating the flame and products of combustion from the process stream. Examples are heat exchangers (dis-

TABLE 27-23 Average Energy Consumption for Various Industries Using Direct Heat

Industry	Product/process	Energy consumption per unit of product	
		GJ/Mg	10^6 Btu/US ton
Paper	Kraft process	20.9	18.0
	Integrated plant/paper*	34.2	29.5
	Integrated plant/paperboard*	18.8	16.2
Glass	Flat glass	17.3	14.9
	Container glass	18.1	15.6
	Pressed/blown	31.6	27.2
Clay/ceramics	Portland cement	4.6	4.0
	Lime	5.5	4.7
	Mineral wool	42.7	36.8
Steel	Blast furnace and steel mills	20.7	17.8
Nonferrous metals	Primary copper	34.2	29.5
	Secondary copper	4.6	4.0
	Primary lead	25.1	21.6
	Secondary lead	0.8	0.7
	Primary zinc	69.6	60.0
	Secondary zinc	5.0	4.3
	Primary aluminum	78.9	68.0
	Secondary aluminum	5.2	4.5

SOURCE: *Manufacturing Consumption of Energy,* Energy Information Administration, U.S. Dept. of Energy, 1991.
*Mixture of direct and indirect firing.

cussed in Sec. 11), steam boilers, fired heaters, muffle furnaces, and melting pots. Steam boilers have been treated earlier in this section, and a subsequent subsection on industrial furnaces will include muffle furnaces.

Fired heaters differ from other indirect-fired processing equipment in that the process stream is heated by passage through a coil or tubebank enclosed in a furnace. Fired heaters are classified by function and by coil design.

Function Berman (*Chem. Eng.* **85**(14): 98–104, June 19, 1978) classifies fired heaters into the following six functional categories, providing descriptions that are abstracted here.

Column reboilers heat and partially vaporize a recirculating stream from a fractionating column. The outlet temperature of a reboiler stream is typically 477 to 546 K (400 to 550°F).

Fractionator-feed preheaters partially vaporize charge stock from an upstream unfired preheater en route to a fractionating column. A typical refinery application: a crude feed to an atmospheric column enters the fired heater as a liquid at 505 K (450°F) and leaves at 644 K (700°F), having become 60 percent vaporized.

Reactor-feed-stream preheaters heat the reactant stream(s) for a high-temperature chemical reaction. The stream may be single-phase/single-component (example: steam being superheated from 644 to 1089 K [700 to 1500°F] for styrene-manufacture reactors); single-phase/multicomponent (example: preheating the feed to a catalytic reformer, a mixture of hydrocarbon vapors and recycle hydrogen, from 700 to 811 K [800 to 1000°F] under pressure as high as 4.1 MPa [600 psia]); or multiphase/multicomponent (example: a mixture of hydrogen gas and liquid hydrocarbon heated from 644 to 727 K [700 to 850°F] at about 20 MPa [3000 psia] before it enters a hydrocracker).

Heat-transfer-fluid heaters maintain the temperature of a circulating liquid heating medium (e.g., a paraffinic hydrocarbon mixture, a Dowtherm, or a molten salt) at a level that may exceed 673 K (750°F).

Viscous-liquid heaters lower the viscosity of very heavy oils to pumpable levels.

Fired reactors contain tubes or coils in which an endothermic reaction within a stream of reactants occurs. Examples include steam/hydrocarbon reformers, catalyst-filled tubes in a combustion chamber; pyrolyzers, coils in which alkanes (from ethane to gas oil) are cracked to olefins; in both types of reactor the temperature is maintained up to 1172 K (1650°F).

Coil Design Indirect-fired equipment is conventionally classified by tube orientation: vertical and horizontal. Although there are many variations of each of these two principal configurations, they all are embraced within seven major types, as follows.

A *simple vertical cylindrical* heater has vertical tubes arrayed along the walls of a combustion chamber fired vertically from the floor. This type of heater does not include a convection section and is inexpensive. It has a small footprint but low efficiency, and it is usually selected for small-duty applications (0.5 to 21 GJ/h [0.5 to 20 10^6 Btu/h]).

Vertical cylindrical; cross-tube convection heaters are similar to the preceding type except for a horizontal convective tube bank above the combustion chamber. The design is economical with a high efficiency and is usually selected for higher-duty applications: 11 to 210 GJ/h (10 to 200 10^6 Btu/h).

The *arbor (wicket)* heater is a substantially vertical design in which the radiant tubes are inverted U's connecting the inlet and outlet terminal manifolds in parallel. An overhead crossflow convection bank is usually included. This type of design is good for heating large gas flows with low pressure drop. Typical duties are 53 to 106 GJ/h (50 to 100 10^6 Btu/h).

In the *vertical-tube single-row double-fired* heater, a single row of vertical tubes is arrayed along the center plane of the radiant section that is fired from both sides. Usually this type of heater has an overhead horizontal convection bank. Although it is the most expensive of the fired heater designs, it provides the most uniform heat transfer to the tubes. Duties are 21 to 132 GJ/h (20 to 125 10^6 Btu/h) per cell (twin-cell designs are not unusual).

Horizontal-tube cabin heaters position the tubes of the radiant-section-coil horizontally along the walls and the slanting roof for the length of the cabin-shaped enclosure. The convection tube bank is placed horizontally above the combustion chamber. It may be fired from the floor, the side walls, or the end walls. As in the case of its vertical cylindrical counterpart, its economical design and high efficiency make it the most popular horizontal-tube heater. Duties are 11 to 105 GJ/h (10 to 100 10^6 Btu).

In the *horizontal-tube box heater with side-mounted convection tube bank,* the radiant-section tubes run horizontally along the walls and the flat roof of the box-shaped heater, but the convection section is placed in a box of its own beside the radiant section. Firing is horizontal from the end walls. The design of this heater results in a relatively expensive unit justified mainly by its ability to burn low-grade high-ash fuel oil. Duties are 53 to 210 GJ/h (50 to 200 10^6 Btu/h).

Vertical cylindrical helical coil heaters are hybrid designs that are classified as vertical heaters, but their in-tube characteristics are like those of horizontal heaters. There is no convection section. In addition to the advantages of simple vertical cylindrical heaters, the helical coil heaters are easy to drain. They are limited to small-duty applications: 5 to 21 GJ/h (5 to 20 10^6 Btu/h).

Schematic elevation sections of a vertical cylindrical, cross-tube convection heater; a horizontal-tube cabin heater; and a vertical cylindrical, helical-coil heater are shown in Fig. 27-51. The seven basic designs and some variations of them are pictured and described in the reference cited above and by R. K. Johnson (*Combustion* **50**(5): 10–16, November 1978).

The design of both radiant and convection sections of fired heaters, along with some equipment descriptions and operating suggestions, are discussed by Berman in *Encyclopedia of Chemical Processing and Design* (McKetta [ed.], vol. 22, Marcel Dekker, 1985, pp. 31–69). He also treats construction materials, mechanical features, and operating points in three other *Chemical Engineering* articles (all in vol. 85 (1978): no. 17, July 31, pp. 87–96; no. 18, August 14, pp. 129–140; and no. 20, Sept. 11, pp. 165–169).

INDUSTRIAL FURNACES

Industrial furnaces serve the manufacturing sector and can be divided into two groups. Boiler furnaces, which are the larger group and are used solely to generate steam, were discussed earlier in the subsection on industrial boilers. Furnaces of the other group are classified as follows: by (1) source of heat (fuel combustion or electricity), (2) func-

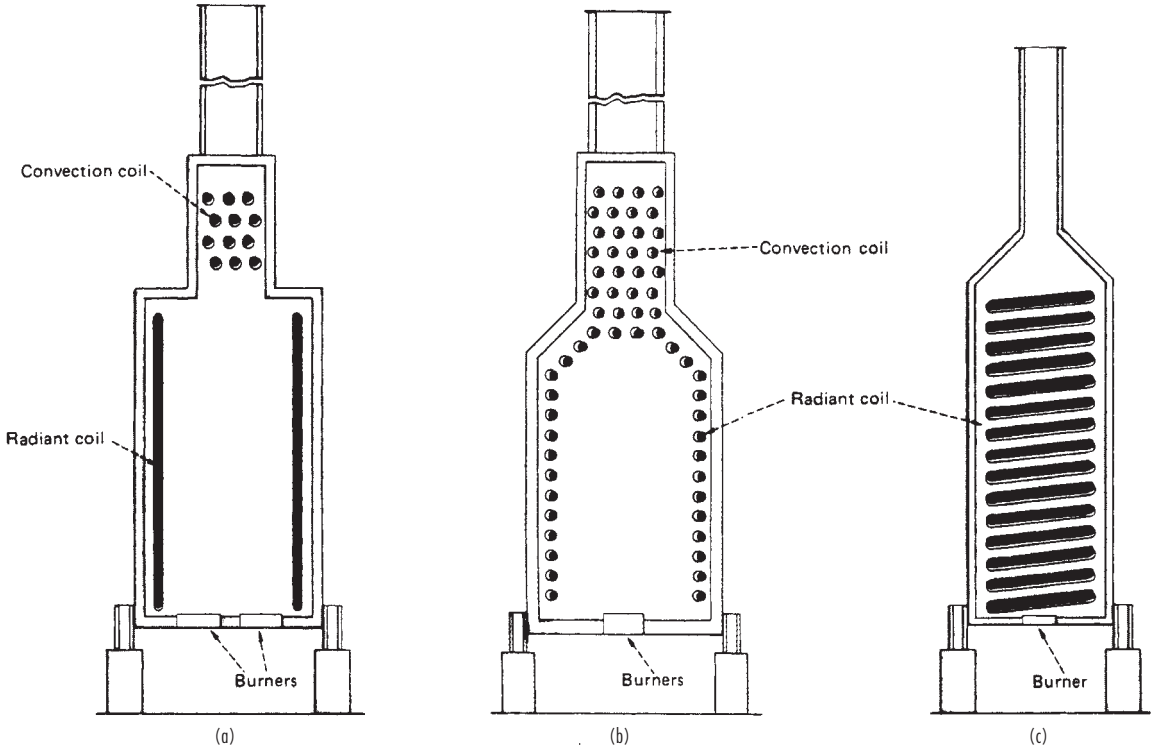


FIG. 27-51 Representative types of fired heaters: (*a*) vertical-tube cylindrical with cross-flow-convection section; (*b*) horizontal-tube cabin; (*c*) vertical cylindrical, helical coil. (*From Berman,* Chem. Eng. ***85:*** *98–104, June 19, 1978.*)

tion (heating without change of phase or with melting), (3) process cycle (batch or continuous), (4) mode of heat application (direct or indirect), and (5) atmosphere in furnace (air, protective, or reactive, including vacuum). Each will be discussed briefly.

Source of Heat Industrial furnaces are either fuel-fired or electric, and the first decision that a prospective furnace user must make is between these two. Although electric furnaces are uniquely suited to a few applications in the chemical industry (manufacture of silicon carbide, calcium carbide, and graphite, for example), their principal use is in the metallurgical and metal-treatment industries. In most cases the choice between electric and fuel-fired is economic or custom-dictated, because most tasks that can be done in one can be done equally well in the other. Except for an occasional passing reference, electric furnaces will not be considered further here. The interested reader will find useful reviews of them in *Kirk-Othmer Encyclopedia of Chemical Technology* (4th ed., vol. 12, articles by Cotchen, Sommer, and Walton, pp. 228–265, Wiley, New York, 1994) and in *Marks' Standard Handbook for Mechanical Engineers* (9th ed., article by Lewis, pp. 7.59–7.68, McGraw-Hill, New York, 1987).

Function and Process Cycle Industrial furnaces are enclosures in which process material is heated, dried, melted, and/or reacted. Melting is considered a special category because of the peculiar difficulties that may be associated with a solid feed, a hot liquid product, and a two-phase mixture in between; it is customary, therefore, to classify furnaces as heating or melting.

Melting Furnaces: The Glass Furnace Most melting furnaces, electric or fuel-fired, are found in the metals-processing industry, but a notable exception is the glass furnace. Like most melting furnaces, a glass furnace requires highly radiative flames to promote heat transfer to the feed charge and employs regenerators to conserve heat from the high-temperature process (greater than 1813 K [2300°F]).

A typical side-port continuous regenerative glass furnace is shown in Fig. 27-52. Side-port furnaces are used in the flat and container glass industries. The burners are mounted on both sides of the furnace and the sides fire alternately. Refractory-lined flues are used to recover the energy of the hot flue gas. The high temperature of the flue gas leaving the furnace heats a mass of refractory material called a *checker.* After the checker has reached the desired temperature, the gas flow is reversed and the firing switches to the other side of the furnace. The combustion air is then heated by the hot checker and can reach 1533 K (2300°F). The cycle of air flow from one checker to the other is reversed approximately every 15 to 30 minutes.

The glass melt is generally 1 to 2 m (3 to 6 ft) deep, the depth being limited by the need for proper heat transfer to the melt. Container glass furnaces are typically 6 to 9 m (20 to 30 ft) wide and 6 to 12 m (20 to 40 ft) long. Flat glass furnaces tend to be longer, typically over 30 m (100 ft), because of the need for complete reaction of the batch ingredients and improved quality (fewer bubbles). They typically have a melting capacity of 450 to 630 Mg/day (500 to 750 US ton/d), compared to a maximum of 540 Mg/day (600 US ton/d) for container and pressed/blown glass furnaces.

Though the stoichiometric chemical energy requirement for glassmaking is only some 2.3 GJ/Mg (2 10^6 Btu/US ton) of glass, the inherently low thermal efficiency of regenerative furnaces means that, in practice, at least 7 GJ/Mg (6 10^6 Btu/US ton) is required. Of this total, some 40 percent goes to batch heating and the required heat of reactions, 30 percent is lost through the furnace structure, and 30 percent is lost through the stack. The smaller furnaces used in pressed/blown glass melting are less efficient, and energy consumption may be as high as 17.4 TJ/Mg (15 10^6 Btu/US ton).

Industrial furnaces may be operated in batch or continuous mode.

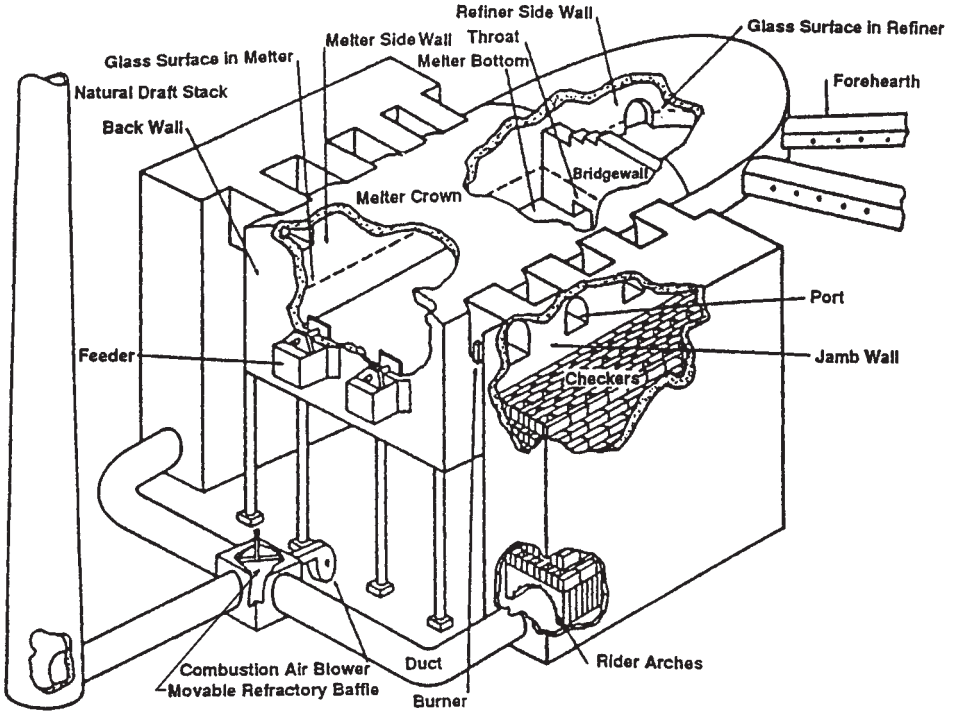


FIG. 27-52 Side-port continuous regenerative glass melting furnace.

Batch Furnaces This type of furnace is employed mainly for the heat treatment of metals and for the drying and calcination of ceramic articles. In the chemical process industry, batch furnaces may be used for the same purposes as batch-tray and truck dryers when the drying or process temperature exceeds 600 K (620°F). They are employed also for small-batch calcinations, thermal decompositions, and other chemical reactions which, on a larger scale, are performed in rotary kilns, hearth furnaces, and shaft furnaces.

Continuous Furnaces These furnaces may be used for the same general purposes as are the batch type, but usually not on small scale. The process material may be carried through the furnace by a moving conveyor (chain, belt, roller), or it may be pushed through on idle rollers, the motion being sustained by an external pusher operating on successively entering cars or trays, each pushing the one ahead along the entire length of the furnace and through the exit flame curtains or doors.

Furnace Atmosphere and Mode of Heating

Direct Heating Industrial furnaces may be directly or indirectly heated, and they may be filled with air or a protective atmosphere, or under a vacuum. Direct heating is accomplished by the hot combustion gases being inside the furnace and therefore in direct contact with the process material. Thus, the material is heated by radiation and convection from the hot gas and by reradiation from the heated refractory walls of the chamber. Three styles of direct firing are illustrated in Fig. 27-53. *Simple direct firing* is used increasingly because of its simplicity and because of improved burners. The *overhead* design allows the roof burners to be so placed as to provide optimum temperature distribution in the chamber. *Underfiring* offers the advantage of the charge's being protected from the flame. The maximum temperature in these direct-heated furnaces is limited to about 1255 K (1800°F) to avoid prohibitively shortened life of the refractories in the furnace.

Indirect Heating If the process material cannot tolerate exposure to the combustion gas or if a vacuum or an atmosphere other than air is needed in the furnace chamber, indirect firing must be employed. This is accomplished in a muffle* furnace or a radiant-tube furnace (tubes carrying the hot combustion gas run through the furnace).

* A *muffle* is an impenetrable ceramic or metal barrier between the firing chamber and the interior of the furnace. It heats the process charge by radiation and furnace atmosphere convection.

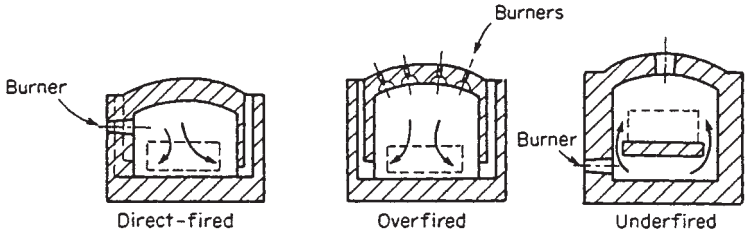


FIG. 27-53 Methods of firing direct-heated furnaces. (*From* Marks' Standard Handbook for Mechanical Engineers, *9th ed., McGraw-Hill, New York, 1987. Reproduced with permission.*)

Atmosphere Protective atmosphere within the furnace chamber may be essential, especially in the heat treatment of metal parts. Mawhinney (in *Marks' Standard Handbook for Mechanical Engineers,* 9th ed., McGraw-Hill, New York, 1987, p. 752) lists pure hydrogen, dissociated ammonia (a hydrogen/nitrogen mixture), and six other protective reducing gases with their compositions (mixtures of hydrogen, nitrogen, carbon monoxide, carbon dioxide, and sometimes methane) that are codified for and by the metals-treatment industry. In general, any other gas or vapor that is compatible with the temperature and the lining material of the furnace can be provided in an indirect-fired furnace, or the furnace can be evacuated.

COGENERATION

Cogeneration is an energy conversion process wherein heat from a fuel is simultaneously converted to useful thermal energy (e.g., process steam) and electric energy. The need for either form can be the primary incentive for cogeneration, but there must be opportunity for economic captive use or sale of the other. In a chemical plant the need for process and other heating steam is likely to be the primary; in a public utility plant, electricity is the usual primary product.

Thus, a cogeneration system is designed from one of two perspectives: it may be sized to meet the process heat and other steam needs of a plant or community of industrial and institutional users, so that the electric power is treated as a by-product which must be either used on site or sold; or it may be sized to meet electric power demand, and the rejected heat used to supply needs at or near the site. The latter approach is the likely one if a utility owns the system; the former if a chemical plant is the owner.

Industrial use of cogeneration leads to small, dispersed electric-power-generation installations—an alternative to complete reliance on large central power plants. Because of the relatively short distances over which thermal energy can be transported, process-heat generation is characteristically an on-site process, with or without cogeneration.

Cogeneration systems will not match the varying power and heat demands at all times for most applications. Thus, an industrial cogeneration system's output frequently must be supplemented by the separate on-site generation of heat or the purchase of utility-supplied electric power. If the on-site electric power demand is relatively low, an alternative option is to match the cogeneration system to the heat load and contract for the sale of excess electricity to the local utility grid.

Fuel saving is the major incentive for cogeneration. Since all heat-engine-based electric power systems reject heat to the environment, that rejected heat can frequently be used to meet all or part of the local thermal energy needs. Using reject heat usually has no effect on the amount of primary fuel used, yet it leads to a saving of all or part of the fuel that would otherwise be used for the thermal-energy process. Heat engines also require a high-temperature thermal input, usually receiving the working fluid directly from a heating source; but in some situations they can obtain the input thermal energy as the rejected heat from a higher-temperature process. In the former case, the cogeneration process employs a heat-engine topping cycle; in the latter case, a bottoming cycle is used.

The choice of fuel for a cogeneration system is determined by the primary heat-engine cycle. Closed-cycle power systems which are externally fired—the steam turbine, the indirectly fired open-cycle gas turbine, and closed-cycle gas turbine systems—can use virtually any fuel that can be burned in a safe and environmentally acceptable manner: coal, municipal solid waste, biomass, and industrial wastes are burnable with closed power systems. Internal combustion engines, on the other hand, including open-cycle gas turbines, are restricted to fuels that have combustion characteristics compatible with the engine type and that yield combustion products clean enough to pass through the engine without damaging it. In addition to natural gas, butane, and the conventional petroleum-derived liquid fuels, refined liquid and gaseous fuels derived from shale, coal, or biomass are in this category. Direct-coal-fired internal combustion engines have been an experimental reality for decades but are not yet a practical reality technologically or economically.

There are at least three broad classes of application for topping-cycle cogeneration systems:

- Utilities or municipal power systems supplying electric power and low-grade heat (e.g., 422 K [300°F]) for local district heating systems
- Large residential, commercial, or institutional complexes requiring space heat, hot water, and electricity
- Large industrial operations with on-site needs for electricity and heat in the form of process steam, direct heat, and/or space heat.

Typical Systems All cogeneration systems involve the operation of a heat engine for the production of mechanical work which, in nearly all cases, is used to drive an electric generator. The commonest heat-engine types appropriate for topping-cycle cogeneration systems are:

- Steam turbines (backpressure and extraction configurations)
- Open-cycle (combustion) gas turbines
- Indirectly fired gas turbines: open cycles and closed cycles
- Diesel engines

Each heat-engine type has unique characteristics, making it better suited for some cogeneration applications than for others. For example, engine types can be characterized by:

- Power-to-heat ratio at design point
- Efficiency at design point
- Capacity range
- Power-to-heat-ratio variability
- Off-design (part-load) efficiency
- Multifuel capability

The major heat-engine types are described in terms of these characteristics in Table 27-24.

TABLE 27-24 Cogeneration Characteristics for Heat Engines

Engine type	Size range, MWe/unit	Efficiency at design point	Part-load efficiency	Multifuel capability	Maximum temperature of recoverable heat, °F (°C)*	Recoverable heat, Btu/kWh†	Typical power-to-heat ratio
Steam turbine							
Extraction-condensing type	30–300	0.25–0.30	Fair	Excellent	200 (93)–600 (315)‡	11,000–35,000	0.1–0.3
Backpressure type	20–200	0.20–0.25	Fair	Excellent	200 (93)–600 (315)‡	17,000–70,000	0.05–0.2
Combustion gas turbines	10–100	0.25–0.30	Poor	Poor	1000 (538)–1200 (649)	3000–11,000	0.3–0.45
Indirectly fired gas turbines							
Open-cycle turbines	10–85	0.25–0.30	Poor	Good	700 (371)–900 (482)	3500–8500	0.4–1.0
Closed-cycle turbines	5–350	0.25–0.30	Excellent	Good	700 (371)–900 (482)	3500–8500	0.4–1.0
Diesel engines	0.05–25	0.35–0.40	Good	Fair to poor	500 (260)–700 (371)	4000–6000	0.6–0.85

*°C + 273 = K
†1 Btu = 1055 J.
‡Saturated steam.

HEAT RECOVERY

REGENERATION

Storage of heat is a temporary operation since perfect thermal insulators are unknown; thus, heat is absorbed in solids or liquids as sensible or latent heat to be released later at designated times and conditions. The collection and release of heat can be achieved in two modes: on a batch basis, as in the checkerbrick regenerator for blast furnaces, or on a continuous basis, as in the Ljungstrom air heater.

Checkerbrick Regenerators Preheating combustion air in open-hearth furnaces, ingot-soaking pits, glass-melting tanks, by-product coke ovens, heat-treating furnaces, and the like has been universally carried out in regenerators constructed of fireclay, chrome, or silica bricks of various shapes. Although many geometric arrangements have been used in practice, the so-called basketweave design has been adopted in most applications.

Blast-Furnace Stoves Blast-furnace stoves are used to preheat the air that is blown into a blast furnace. A typical blast furnace, producing 1500 Mg (1650 US ton) of pig iron per day, will be blown with 47.2 m^3/s (100,000 std ft^3/min) of atmospheric air preheated to temperatures ranging in normal practice from 755 to 922 K (900 to 1200°F). A set of four stoves is usually provided, each consisting of a vertical steel cylinder 7.3 m (24 ft) in diameter, 33 m (108 ft) high, topped with a spherical dome. Characteristic plan and elevation sections of a stove are shown in Fig. 27-54. The interior comprises three regions: in the cylindrical portion, (1) a side combustion chamber, lens-shaped in cross section, bounded by a segment of the stove wall and a mirror-image bridgewall separating it from (2) the chamber of the cylinder that is filled with heat-absorbing checkerbrick, and (3) the capping dome, which constitutes the open passage between the two chambers.

The heat-exchanging surface in each stove is just under 11,500 m^2 (124,000 ft^2). In operation, each stove is carried through a two-step 4-h cycle. In a 3-h *on-gas* step, the checkerbricks in a stove are heated by the combustion of blast-furnace gas. In the alternating *on-wind* 1-h step, they are cooled by the passage of cold air through the stove. At any given time, three stoves are simultaneously on gas, while a single stove is on wind.

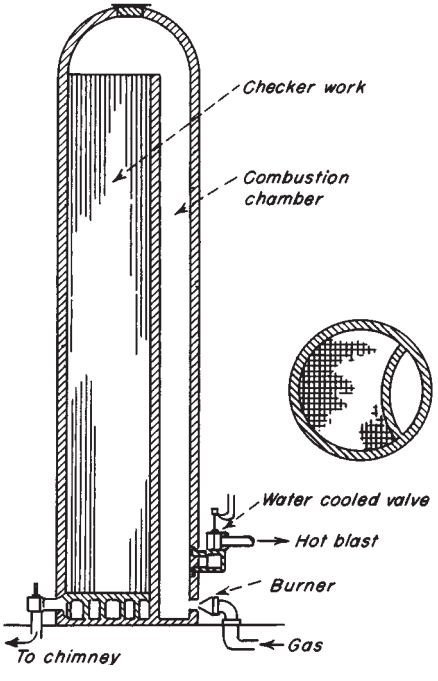


FIG. 27-54 Blast-furnace stove.

At the start of an on-wind step, about one-half of the air, entering at 366 K (200°F), passes through the checkerbricks, the other half being bypassed around the stove through the cold-blast mixer valve. The gas passing through the stove exhausts at 1366 K (2000°F). Mixing this with the unheated air produces a blast temperature of 811 K (1000°F). The temperature of the heated air from the stove falls steadily throughout the on-wind step. The fraction of total air volume bypassed through the mixer valve is continually decreased by progressively closing this valve, its operation being automatically regulated to maintain the exit gas temperature at 811 K. At the end of 1 h of on-wind operation, the cold-blast mixer valve is closed, sending the entire blast through the checkerbricks.

Open-Hearth and Glass-Tank Regenerators These contain checkerbricks that are modified considerably from those used in blast-furnace stoves because of the higher working temperatures, more drastic thermal shock, and dirtier gases encountered. Larger bricks form flue cross sections five times as large as the stove flues, and the percentage of voids in the checkerbricks is 51 percent, in contrast to 32 percent voids in stoves. The vertical height of the flues is limited by the elevation of the furnace above plant level. Short flues from 3 to 4.9 m (10 to 16 ft) are common in contrast to the 26- to 29-m (85- to 95-ft) flue lengths in blast-furnace stoves.

As a result of the larger flues and the restricted surface area per unit of gas passed, regenerators employed with this type of furnace exhibit much lower efficiency than would be realized with smaller flues. In view of the large amount of iron oxide contained in open-hearth exhaust gas and the alkali fume present in glass-tank stack gases, however, smaller checkerbrick dimensions are considered impractical.

Ljungstrom Heaters A familiar continuous regenerative-type air heater is the Ljungstrom heater (Fig. 27-55). The heater assembly consists of a slow-moving rotor embedded between two peripheral housings separated from one another by a central partition. Through one side of the partition a stream of hot gas is being cooled, and, through the other side a stream of cold gas is being heated. Radial and circumferential seals sliding on the rotor limit the leakage between the streams. The rotor is divided into sectors, each of which is tightly packed with metal plates and wires that promote high heat-transfer rates at low pressure drop.

These heaters are available with rotors up to 6 m (20 ft) in diameter. Gas temperatures up to 1255 K (1800°F) can be accommodated. Gas face velocity is usually around 2.5 m/s (500 ft/min). The rotor height depends on service, efficiency, and operating conditions but usually is between 0.2 and 0.91 m (8 and 36 in). Rotors are driven by small motors with rotor speed up to 20 r/min. Heater effectiveness can be as high as 85 to 90 percent heat recovery. Lungstrom-type heaters are used in power-plant boilers and also in the process industries for heat recovery and for air-conditioning and building heating.

Regenerative Burners In these systems a compact heat storage regenerator (containing ceramic balls, for example) is incorporated into the burner. Operating in pairs, one burner fires while the other exhausts: combustion air is preheated in the regenerator of the firing burner and furnace gas gives up heat to the regenerator in the exhausting burner (see Fig. 27-56). Burner operations are switched periodically. Such systems can yield combustion air preheats between 933 K (1220°F) and 1525 K (2282°F) for furnace temperature between 1073 K (1472°F) and 1723 K (2642°F), respectively. Corresponding fuel savings compared to cold-air firing will vary approximately from 30 to 70 percent.

Miscellaneous Systems Many other systems have been proposed for transferring heat regeneratively, including the use of high-temperature liquids and fluidized beds for direct contact with gases, but other problems which limit industrial application are encountered. These systems are covered by methods described in Secs. 11 and 12 of this handbook.

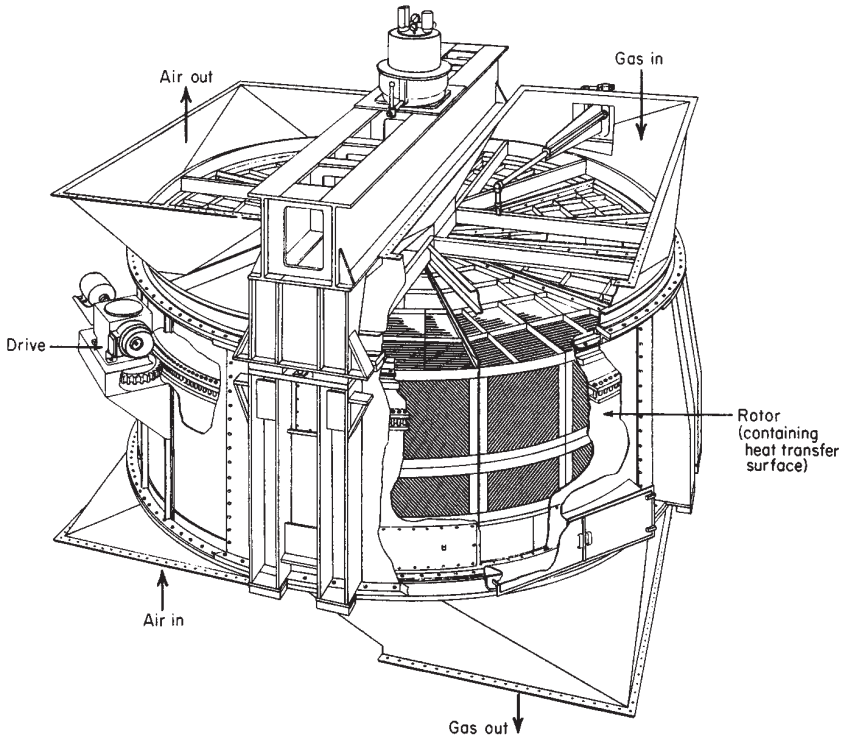


FIG. 27-55 Ljungstrom air heater.

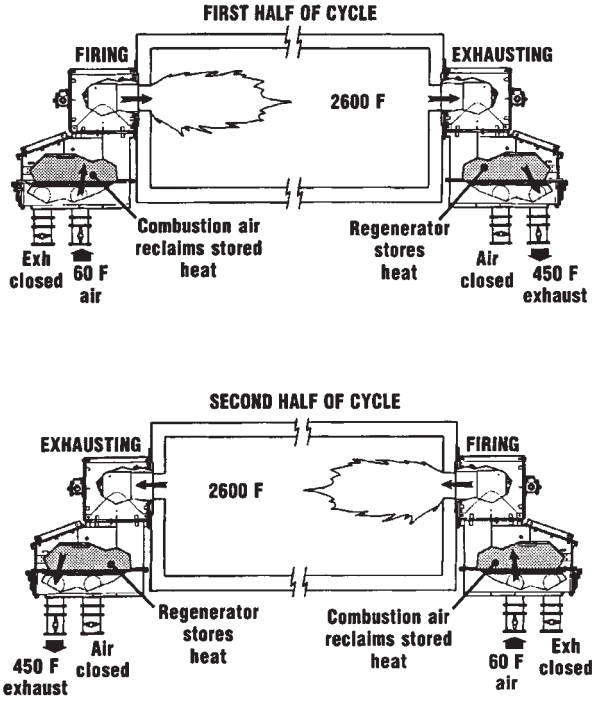


FIG. 27-56 Schematic of a regenerative burner system. (*North American Manufacturing Co.*)

RECUPERATORS

Regenerators are by nature intermittent or cycling devices, although, as set forth previously, the Ljunstrom design avoids interruption of the fluid stream by cycling the heat-retrieval reservoir between the hot and cold fluid streams. Truly continuous counterparts of regenerators exist, however, and they are called *recuperators.*

The simplest configuration for a recuperative heat exchanger is the metallic radiation recuperator (Fig. 27-57). The inner tube carries the hot exhaust gases and the outer tube carries the combustion air. The bulk of the heat transfer from the hot gases to the surface of the inner tube is by radiation, whereas that from the inner tube to the cold combustion air is predominantly by convection.

Shell-and-tube heat exchangers (see Sec. 11) may also be used as recuperators; convective heat transfer dominates in these recuperators. An alternative arrangement for a convective-type recuperator is shown in Fig. 27-58 (the dimpled end of the tube serves to ensure that there is adequate heat transfer from the cool fluid internally and that the tube bottom does not overheat and fail). For applications involving higher temperatures, ceramic recuperators have been developed. These devices can allow operation at up to 1823 K (2822°F) on the gas side and over 1093 K (1508°F) on the air side. Early ceramic recuperators were built of furnace brick and cement, but the repeated thermal cycling caused cracking and rapid deterioration of the recuperator. Later designs have used various approaches to overcome the problems of leakage and cracking, one of which is shown in Fig. 27-59. Silicon carbide tubes carry the combustion air through the waste gas, and flexible seals are used in the air headers. In this manner, the seals are maintained at comparatively low temperatures and the leakage rate can be reduced to a few percent of the total flow.

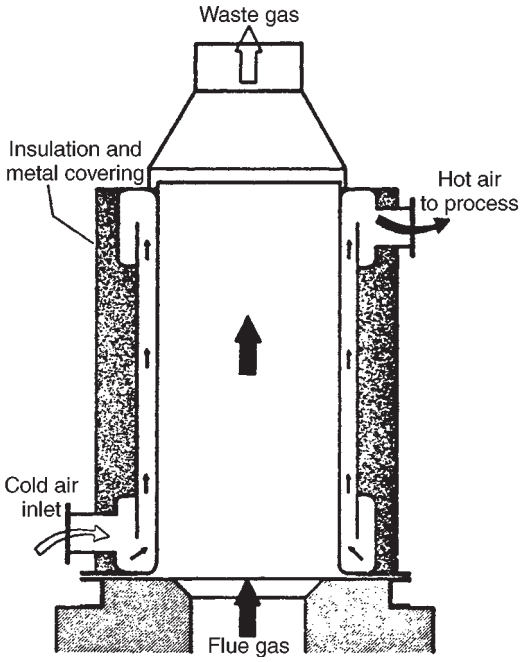


FIG. 27-57 Diagram of a metallic radiation recuperator. (*From Goldstick & Thumann,* Principles of Waste Heat Recovery, *Fairmont Press, Atlanta, 1986.*)

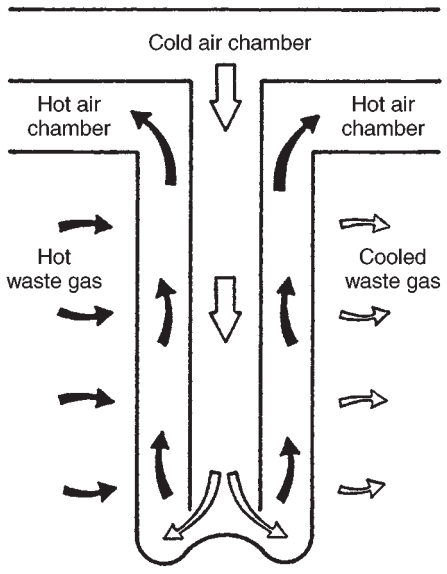


FIG. 27-58 Diagram of a vertical tube-within-tube recuperator. (*From Goldstick & Thumann,* Principles of Waste Heat Recovery, *Fairmont Press, Atlanta, 1986.*)

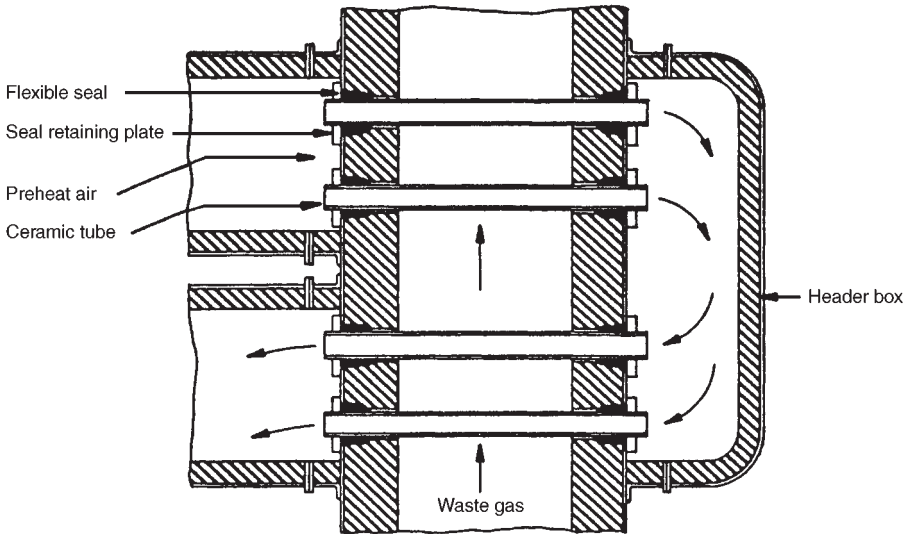


FIG. 27-59 Ceramic recuperator. In this design the seals are maintained at relatively low temperatures, leading to leakage rates of only a few percent. (*From Goldstick & Thumann,* Principles of Waste Heat Recovery, *Fairmont Press, Atlanta, 1986.*)

ELECTROCHEMICAL ENERGY CONVERSION

Electricity has become as indispensable as heat to the functioning of industrialized society. The source of most of the electricity used is the energy of the fuels discussed earlier in this section: liberated by combustion as heat, it drives heat engines which, in turn, drive electrical generators.

In some instances, however, part of the chemical energy bound in relatively high-enthalpy compounds can be converted directly to electricity as these reactants are converted to products of lower enthalpy (galvanic action). A process in the opposite direction also is possible for some systems: an electric current can be absorbed as the increased chemical energy of the higher-enthalpy compounds (electrolytic action). The devices in which electrochemical energy conversion processes occur are called cells.

Galvanic cells in which stored chemicals can be reacted on demand to produce an electric current are termed *primary cells.* The discharging reaction is irreversible and the contents, once exhausted, must be replaced or the cell discarded. Examples are the dry cells that activate small appliances. In some galvanic cells (called *secondary cells*), however, the reaction is reversible: that is, application of an electrical potential across the electrodes in the opposite direction will restore the reactants to their high-enthalpy state. Examples are rechargeable batteries for household appliances, automobiles, and many industrial applications. Electrolytic cells are the reactors upon which the electrochemical process, electroplating, and electrowinning industries are based.

Detailed treatment of the types of cells discussed above is beyond the scope of this handbook. For information about electrolytic cells, interested readers are referred to Fuller, Newman, Grotheer, and King ("Electrochemical Processing," in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 9, Wiley, New York, 1994, pp. 111–197) and for primary and secondary cells, to Crompton (*Battery Reference Book,* 2d ed., Butterworth-Heineman, Oxford, U.K., 1995). Another type of cell, however, a galvanic cell to which the reactants of an exothermic reaction are fed continuously, in which they react to liberate part of their enthalpy as electrical energy, and from which the products of the reaction are discharged continuously, is called a *fuel cell.* Fuel cell systems for generating electricity in a variety of applications are being commercialized by a number of companies. The rest of this section is devoted to a discussion of fuel cell technology.

FUEL CELLS

General References: Appleby and Foulkes, *Fuel Cell Handbook,* Kreger Publishing Co., Molabar, Fla., 1993. Hirschenhofer, Staufer, and Engleman, *Fuel Cell Handbook* (Rev. 3), U.S. Dept. of Energy, Morgantown Energy Technology Center, DOE/METC-94/1006, Morgantown, W. Va., 1994. Kinoshita and Cairns, "Fuel Cells," in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 11, Wiley, New York, 1994, p. 1098. Liebhafsky and Cairns, *Fuel Cells and Fuel Batteries,* Wiley, New York, 1968. Linden (ed.), *Handbook of Batteries and Fuel Cells,* McGraw-Hill, New York, 1984.

Background Energy conversion in fuel cells is direct and simple when compared to the sequence of chemical and mechanical steps in heat engines. A fuel cell consists of an anode, an electrolyte, and a cathode. On the anode, the fuel is oxidized electrochemically to positively charged ions. On the cathode, oxygen molecules are reduced to oxide or hydroxide ions. The electrolyte serves to transport either the positively charged or negatively charged ions from anode to cathode or cathode to anode. Figure 27-60 is a schematic representation of the reactions in a fuel cell operating on hydrogen and air with a hydrogen-ion-conducting electrolyte. The hydrogen flows over the anode, where the molecules are separated into ions and electrons. The ions migrate through the ionically conducting but electronically insulating electrolyte to the cathode, and the electrons flow through the outer circuit energizing an electric load. The electrons combine eventually with oxygen molecules flowing over the surface of the cathode and hydrogen ions migrating across the electrolyte, forming water, which leaves the fuel cell in the depleted air stream.

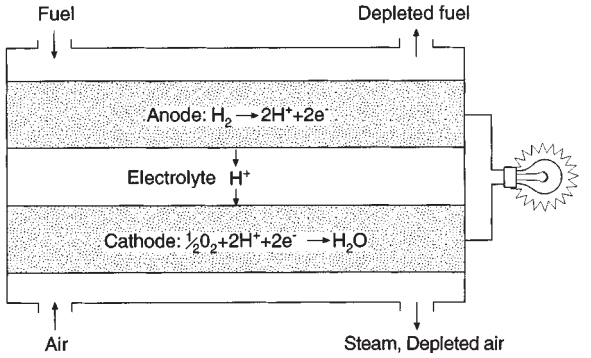


FIG. 27-60 Fuel cell schematic.

A fuel cell has no moving parts. It runs quietly, does not vibrate, and does not generate gaseous pollutants. The idea of the fuel cell is generally credited to Sir William Grove, who lived in the nineteenth century. It took over 100 years for the first practical devices to be built, in the U.S. space program, as the power supply for space capsules and the space shuttle. Commercialization of terrestrial fuel cell systems is beginning only now. Having lower emissions and being more efficient than heat engines, fuel cells may in time become the power source for a broad range of applications, beginning with utility power plants, including civilian and military transportation, and reaching into portable electronic devices.

This slow realization of the concept is due to the very demanding materials requirements for fuel cells. The anodes and cathodes have to be good electronic conductors and must have electrocatalytic properties to facilitate the anodic and cathodic reactions. In addition, the anodes and cathodes must be porous to allow the fuel and oxidant gases to diffuse to the reaction sites, yet they must be mechanically strong enough to support the weight of the fuel cell stacks. The electrolyte must be chemically stable in hydrogen and oxygen, and must have an ionic conductivity of at least 0.1 S/cm. Five classes of electrolytes have been found to meet these requirements: potassium hydroxide, phosphoric acid, perfluorinated sulfonic acid resins, molten carbonates, and oxide-ion-conducting ceramics. Consequently, five types of fuel cell based on these electrolytes have been developed.

Fuel Cell Efficiency The theoretical energy conversion efficiency of a fuel cell $\varepsilon°$ is given by the ratio of the free energy (Gibbs function) of the cell reaction at the cell's operating temperature ΔG_t to the enthalpy of reaction at the standard state $\Delta H°$, both quantities being based on a mole of fuel:

$$\varepsilon° = \frac{\Delta G_t}{\Delta H°} \tag{27-50}$$

The enthalpy of reaction is always taken at a temperature of 298 K (77°F), but the product water can be either liquid or gaseous. If it is liquid, the efficiency is based on the higher heating value (HHV), but if the product is gaseous, the efficiency is based on the lower heating value (LHV). If the fuel cell runs on hydrogen and oxygen at 373 K (212°F), the theoretical conversion efficiency is 91 percent LHV or 83 percent HHV. The theoretical efficiency of fuel cells as given in Eq. (27-50) is equivalent to the Carnot efficiency of heat engines with the working medium absorbing heat at the flame temperature of the fuel and rejecting it at 298 K. Owing to materials and engineering limitations, heat engines cannot operate at the Carnot limit. Fuel cells can run at efficiencies near the theoretical values but only at low power density (power produced per unit of active fuel cell area). At higher power densities, the efficiency of fuel cells is constrained by electrical resistances within the bulk and at the interfaces of the materials, and by gas diffusion losses.

TABLE 27-25 Thermodynamic Values for $H_2 + \frac{1}{2}O_2 = H_2O$ (g)

Temperature, K	Enthalpy of reaction ($\Delta H°$), kJ/mol	Free energy of reaction ($\Delta G°$), kJ/mol	Equilibrium cell potential ($E°$), V
300	−241.8	−228.4	1.18
500	−243.9	−219.2	1.14
700	−245.6	−208.8	1.06
900	−247.3	−197.9	1.03
1100	−248.5	−187.0	0.97
1300	−249.4	−175.7	0.91

When no net current is flowing, the equilibrium potential of the fuel cell is given by the Nernst equation:

$$E° = \frac{-\Delta G_t}{nF} \tag{27-51}$$

where $E°$ is the electrochemical equilibrium potential, V; n is the number of electrons transferred in the cell reaction (equivalents), and F is the Faraday constant. If the units of ΔG_t are J/mol, F has the value 96,487 C/mol·equiv. The potential depends on the chemical species of the fuel and the operating temperature. For hydrogen and oxygen, variation of the equilibrium cell potential with temperature is shown in Table 27-25.

When current is flowing, the actual cell operating potential is given by:

$$E = E° - (a_{an} + a_{ca}) - (b_{an} + b_{ca}) \frac{RT}{nF} \ln i - Ai \tag{27-52}$$

where a and b are characteristic constants for the electrochemical reactions at the electrode materials; the subscripts an and ca refer to the anode and the cathode, respectively; R is the gas constant; T is the cell temperature; A is the area-specific resistance of the fuel cell; and i is the current density (current flow per unit of active fuel cell area) in the cell.

Graphs of operating potential versus current density are called *polarization curves*, which reflect the degree of perfection that any particular fuel cell technology has attained. High cell operating potentials are the result of many years of materials optimization. Actual polarization curves will be shown below for several types of fuel cell.

The actual efficiency of an operating fuel cell is given by:

$$\varepsilon = \frac{-nFE}{\Delta H°} U_f \tag{27-53}$$

where U_f is the electrochemical fuel utilization (amount of fuel converted divided by amount fed to the cell). For pure hydrogen the fuel utilization can be 1.0, but for gas mixtures it is often 0.85. Equations (27-52) and (27-53) show that the efficiency of fuel cells is not constant, but depends on the current density. The more power that is drawn, the lower the efficiency.

When the fuel gas is not pure hydrogen and air is used instead of pure oxygen, additional adjustment to the calculated cell potential becomes necessary. Since the reactants in the two gas streams practically become depleted between the inlet and exit of the fuel cell, the cell potential is decreased by a term representing the log mean fugacities, and the operating cell efficiency becomes:

$$\varepsilon_{fc} = \frac{nFU_f}{\Delta H°}\left[E° - \sum a - \sum b \frac{RT}{nF} \ln i - A\, i\right] - \frac{RTU_f}{\Delta H°}\left[\nu_f \ln(\text{log mean } \hat{f}_f) + \nu_{ox} \ln(\text{log mean } \hat{f}_{ox})\right] \tag{27-54}$$

The quantities ν_f and ν_{ox} are the stoichiometric coefficients for the fuel cell reaction, and $\hat{f}_f$ and $\hat{f}_{ox}$ are the fugacities of fuel and oxygen in their respective streams.

Further, as the current density of the fuel cell increases, a point is inevitably reached where the transport of reactants to or products from the surface of the electrode becomes limited by diffusion. A *concentration polarization* is established at the electrode, which diminishes the cell operating potential. The magnitude of this effect depends on many design and operating variables, and its value must be obtained empirically.

Design Principles An individual fuel cell will generate an electrical potential of about 1 V or less, as discussed above, and a current that is proportional to the external load demand. For practical applications, the voltage of an individual fuel cell is obviously too small, and cells are therefore stacked up as shown in Fig. 27-61. Anode/electrolyte/cathode assemblies are electrically connected in series by inserting a bipolar plate between the cathode of one cell and the anode of the next. The bipolar plate must be impervious to the fuel

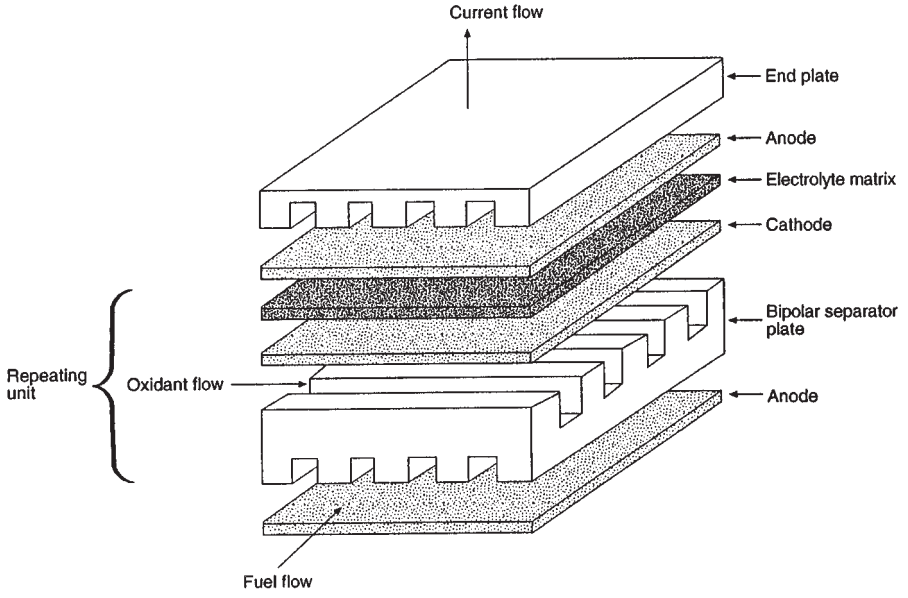


FIG. 27-61 Stacking of individual fuel cells.

and oxidant gases, chemically stable under reducing and oxidizing conditions, and an excellent electronic conductor. In addition, it is often used to distribute the gases to the anode and cathode surfaces through flow channels cut or molded into it.

The number of fuel cells that are stacked is determined by the desired electrical potential. For 110-V systems it can be about 200 cells. Since a typical fuel cell is about 5 mm (0.2 in) thick, a 200-cell stack assembly (including the end hardware that keeps the unit under compression) is about 2 m (6 ft) tall. The reactant and product gas streams are supplied and removed from the stack by external or internal manifolding. Externally manifolded stacks have shallow trays on each of the four sides to supply the fuel and air and to remove the depleted gases and reaction products. The manifolds are mechanically clamped to the stacks and sealed at the edges. These manifold seals must be gastight, electrically insulating, and able to tolerate thermal expansion mismatches between the stack and the manifold materials as well as dimensional changes due to aging.

Alternatively, reactant and product gases can be distributed to and removed from individual cells through internal pipes in a design analogous to that of filter presses. Care must be exercised to assure an even flow distribution between the entry and exit cells. The seals in internally manifolded stacks are generally not subject to electrical, thermal, and mechanical stresses, but are more numerous than in externally manifolded stacks.

Because fuel cells generate an amount of excess heat consistent with their thermodynamic efficiency, they must be cooled. In low-temperature fuel cells, the cooling medium is generally water or oil, which flows through cooling plates interspaced throughout the stack. In high-temperature cells, heat is removed by the reactant air stream and also by the endothermic fuel reforming reactions in the stack.

Types of Fuel Cells The five major types of fuel cell are listed in Table 27-26. Each has unique chemical features. The *alkaline fuel cell* (AFC) has high power density and has proven itself as a reliable power source in the U.S. space program, but the alkaline electrolyte reacts with carbon dioxide, which is present in reformed hydrocarbon fuels and air. The *polymer electrolyte fuel cell* (PEFC) and the *phosphoric acid fuel cell* (PAFC) are compatible with carbon dioxide, but both are sensitive to carbon monoxide (PEFC much more so than PAFC), which is adsorbed onto the platinum catalyst and renders it inactive. Therefore, these three types of fuel cell require pure hydrogen as fuel; and if the hydrogen has been obtained by reforming a fuel such as natural gas, the hydrogen-rich fuel stream must be purified before being introduced into the fuel cell. The *molten carbonate fuel cell* (MCFC) and the *solid oxide fuel cell* (SOFC) can tolerate carbon monoxide and can operate on hydrocarbon fuels with minimal fuel processing, but they operate at elevated temperatures.

The operating temperature also affects the fuel cell operating potential. A high operating temperature accelerates reaction rates but lowers the thermodynamic equilibrium potential. These effects balance one another, and, in practice, the operating point of any fuel cell is usually between 0.7 and 0.8 V. The cell reactions for the five types of fuel cell are summarized in Table 27-27. It is important to note that in cells with acidic electrolytes (PAFC and PEFC) the product water evolves on the air electrode, but in the alkaline ones (AFC, MCFC, and SOFC) it is generated on the fuel electrode. This has consequences for the processing of hydrocarbon fuels, as discussed later.

Following is a summary of the materials, operating characteristics, and mode of construction for each type of fuel cell.

Alkaline Fuel Cell The electrolyte for NASA's space shuttle orbiter fuel cell is 35 percent potassium hydroxide. The cell operates between 353 and 363 K (176 and 194°F) at 0.4 MPa (59 psia) on hydrogen and oxygen. The electrodes contain platinum-palladium and platinum-gold alloy powder catalysts bonded with polytetrafluoroethylene (PTFE) latex and supported on gold-plated nickel screens for current collection and gas distribution. A variety of materials, including asbestos and potassium titanate, are used to form a microporous separator that retains the electrolyte between the electrodes. The cell structural materials, bipolar plates, and external housing are usually nickel, plated to resist corrosion. The complete orbiter fuel cell power plant is shown in Fig. 27-62.

Typical polarization curves for alkaline fuel cells are shown in Fig. 27-63. It is apparent that the alkaline fuel cell can operate at about 0.9 V and 500 mA/cm^2 current density. This corresponds to an energy conversion efficiency of about 60 percent HHV. The space shuttle orbiter power module consists of three separate units, each measuring 0.35 by 0.38 by 1 m (14 by 15 by 40 in), weighing 119 kg (262 lb), and generating 15 kW of power. The power density is about 100 W/L and the specific power, 100 W/kg.

Polymer Electrolyte Fuel Cell The PEFC, also known as the *proton-exchange-membrane fuel cell* (PEMFC), is of much interest because it is capable of high power density and it can deliver about 40 percent of its nominal power at room temperature. These features have made the PEFC a candidate to replace internal combustion engines in transportation applications, and prototype passenger cars with fuel cell power sources have been developed. Methanol, ethanol, hydrogen, natural gas, dimethyl ether, and common transportation fuels such as gasoline are being considered as fuel. All but hydrogen require a reforming step to provide hydrogen for the fuel cell. The

TABLE 27-26 Fuel Cell Characteristics

Type of fuel cell	Electrolyte	Operating temperature, K	Operating temperature, °C	Coolant medium
Alkaline	KOH	363	90	Water
Polymer	$CF_3(CF_2)_nOCF_2SO_3^-$	353	80	Water
Phosphoric acid	H_3PO_4	473	200	Steam/water
Molten carbonate	Li_2CO_3-K_2CO_3	923	650	Air
Solid oxide	$Zr_{0.92}Y_{0.08}0_{1.96}$	1273	1000	Air

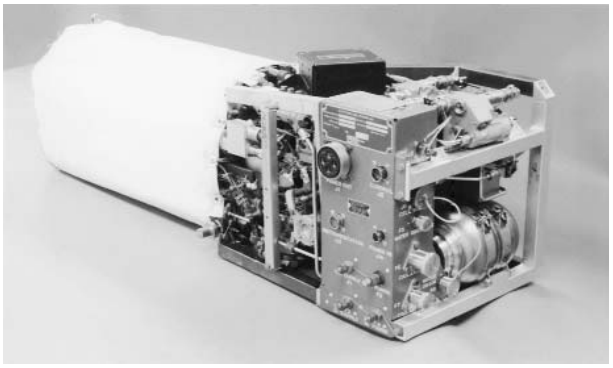


FIG. 27-62 Orbiter power plant. (*International Fuel Cells.*)

TABLE 27-27 Fuel Cell Reaction Electrochemistry

Type of fuel cell	Conducting ion	Anode reaction	Cathode reaction
Alkaline	OH^-	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Polymer	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Phosphoric acid	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Molten carbonate	CO_3^{2-}	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
Solid oxide	O^{2-}	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

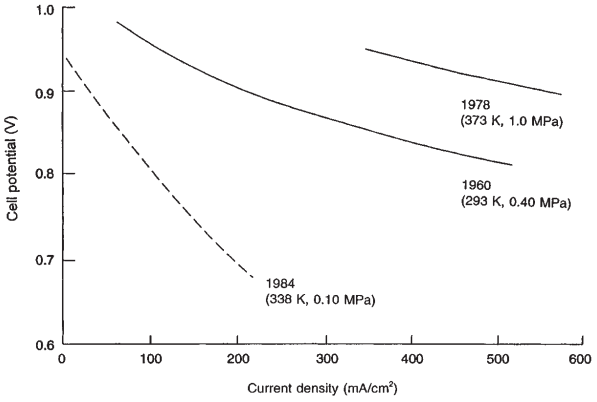


FIG. 27-63 Polarization curves for alkaline fuel cells.

motivation for this development effort is the virtual elimination of both on-road emissions from automobiles and the range limitations associated with battery-powered electric automobiles.

The electrolyte is a perfluorosulfonic acid ionomer, commercially available under the trade name of Nafion™. It is in the form of a membrane about 0.17 mm (0.007 in) thick, and the electrodes are bonded directly onto the surface. The electrodes contain very finely divided platinum or platinum alloys supported on carbon powder or fibers. The bipolar plates are made of graphite or metal.

Typical platinum catalyst loadings needed to support the anodic and cathodic reactions are currently 1 to 2 mg/cm^2 of active cell area. Owing to the cost of platinum, substantial efforts have been made to reduce the catalyst loading, and some fuel cells have operated at a catalyst loading of 0.25 mg/cm^2.

To be ionically conducting, the fluorocarbon ionomer must be "wet": under equilibrium conditions, it will contain about 20 percent water. The operating temperature of the fuel cell must be less than 373 K (212°F), therefore, to prevent the membrane from drying out.

Being acidic, fluorocarbon ionomers can tolerate carbon dioxide in the fuel and air streams; PEFCs, therefore, are compatible with hydrocarbon fuels. However, the platinum catalysts on the fuel and air electrodes are extremely sensitive to carbon monoxide: only a few parts per million are acceptable. Catalysts that are tolerant to carbon monoxide are being explored. Typical polarization curves for PEFCs are shown in Fig. 27-64.

A schematic diagram of a methanol-fueled PEFC system is shown in Fig. 27-65. A methanol reformer (to convert CH_3OH to H_2 and CO_2 as the principal products), a water-gas shift reactor (to convert most of the coproduct CO to CO_2, and to provide additional H_2), and a preferential oxidizer (to reduce the residual CO to 10 ppm) are included in the system.

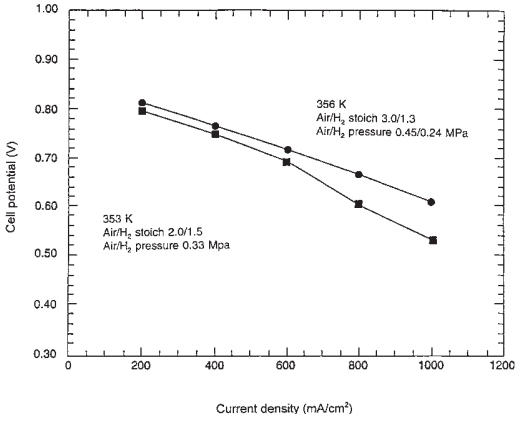


FIG. 27-64 Polarization curves for PEFC stacks.

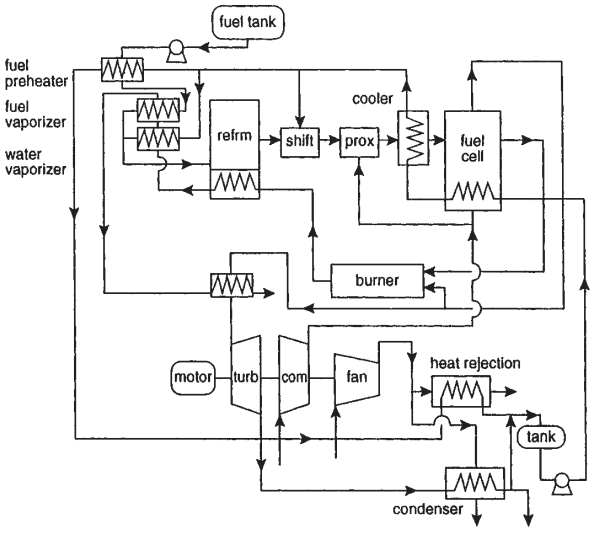


FIG. 27-65 Methanol-fueled PEFC system schematic.

Polymer electrolyte fuel cells can be obtained from several developers. These fuel cells deliver about 5 kW of power and measure 30 by 30 by 70 cm (12 × 12 × 28 in.). For the large production volume anticipated if the automotive industry were to adopt the PEFC, a system cost of less than $100/kW may be reached eventually.

Phosphoric Acid Fuel Cell This type of fuel cell was developed in response to the industry's desire to expand the natural-gas market. The electrolyte is 93 to 98 percent phosphoric acid contained in a matrix of silicon carbide. The electrodes consist of finely divided platinum or platinum alloys supported on carbon black and bonded with PTFE latex. The latter provides enough hydrophobicity to the electrodes to prevent flooding of the structure by the electrolyte. The carbon support of the air electrode is specially formulated for oxidation resistance at 473 K (392°F) in air and positive potentials.

The bipolar plate material of the PAFC is graphite. A portion of it has a carefully controlled porosity that serves as a reservoir for phosphoric acid and provides flow channels for distribution of the fuel and oxidant. The plates are electronically conductive but impervious to gas crossover.

In a typical PAFC system, methane passes through a reformer with steam from the coolant loop of the water-cooled fuel cell. Heat for the reforming reaction is generated by combusting the depleted fuel. The reformed natural gas contains typically 60 percent H_2, 20 percent CO, and 20 percent H_2O. Because the platinum catalyst in the PAFC can tolerate only about 0.5 percent CO, this fuel mixture is passed through a water gas shift reactor before being fed to the fuel cell.

PAFC systems are commercially available from the ONSI Corporation as 200-kW stationary power sources operating on natural gas. The stack cross section is 1 m^2 (10.8 ft^2). It is about 2.5 m (8.2 ft) tall and rated for a 40,000-h life. It is cooled with water/steam in a closed loop with secondary heat exchangers. The photograph of a unit is shown in Fig. 27-66. These systems are intended for on-site power and heat generation for hospitals, hotels, and small businesses. Another application, however, is as "dispersed" 5- to 10-MW power plants in metropolitan areas. Such units would be located at electric utility distribution centers, bypassing the high-voltage transmission system. The market entry price of the system is $3000/kW. As production volumes increase, the price is projected to decline to $1000 to 1500/kW.

Molten Carbonate Fuel Cell The electrolyte in the MCFC is a



FIG. 27-66 PC-25™ commercial 200-kW PAFC generator. (*International Fuel Cells.*)

mixture of lithium/potassium or lithium/sodium carbonates, retained in a ceramic matrix of lithium aluminate. The carbonate salts melt at about 773 K (932°F), allowing the cell to be operated in the 873 to 973 K (1112 to 1292°F) range. Platinum is no longer needed as an electrocatalyst because the reactions are fast at these temperatures. The anode in MCFCs is porous nickel metal with a few percent of chromium or aluminum to improve the mechanical properties. The cathode material is lithium-doped nickel oxide.

The bipolar plates are made from either Type 310 or Type 316 stainless steel, which is coated on the fuel side with nickel and aluminized in the seal area around the edge of the plates. Both internally and externally manifolded stacks have been developed.

In MCFCs, the hydrogen fuel is generated from such common fuels as natural gas or liquid hydrocarbons by steam reforming; the fuel processing function can be integrated into the fuel cell stack because the operating temperature permits reforming using the waste heat. An added complexity in MCFCs is the need to recycle carbon dioxide from the anode side to the cathode side to maintain the desired electrolyte composition. (At the cathode, carbon dioxide reacts with incoming electrons and oxygen in air to regenerate the carbonate ions that are consumed at the anode.) The simplest way is to burn the depleted fuel and mix it with the incoming air. This works well but dilutes the oxygen with the steam generated in the fuel cell. A steam condenser and recuperative heat exchanger can be added to eliminate the steam, but at increased cost.

The fuel cell must be cooled with either water or air, and the heat can be converted to electricity in a bottoming cycle. The dc electrical output of the stack is usually converted to ac and stepped up or down in voltage, depending on the application. Analogous to PAFCs, MCFC stacks are about 1 m^2 (10.8 ft^2) in plan area and quite tall. A stack generates 200 to 300 kW. Market entry is expected in 1999.

Solid Oxide Fuel Cell In SOFCs the electrolyte is a ceramic oxide ion conductor, such as yttrium-doped zirconium oxide. The conductivity of this material is 0.1 S/cm at 1273 K (1832°F); it decreases to 0.01 S/cm at 1073 K (1472°F), and by another order of magnitude at 773 K (932°F). Because the resistive losses need to be kept below about 50 mV, the operating temperature of the SOFC depends on the thickness of the electrolyte. For a thickness of 100 μm or more, the operating temperature is 1273 K (1832°F), but fuel cells with thin electrolytes can operate between 973 and 1073 K (1292 and 1472°F).

The anode material in SOFCs is a cermet (metal/ceramic composite material) of 30 to 40 percent nickel in zirconia, and the cathode is lanthanum manganite doped with calcium oxide or strontium oxide. Both of these materials are porous and mixed ionic/electronic conductors. The bipolar separator typically is doped lanthanum chromite, but a metal can be used in cells operating below 1073 K (1472°F). The bipolar plate materials are dense and electronically conductive.

Typical polarization curves for SOFCs are shown in Fig. 27-67. As discussed earlier, the open-circuit potential of SOFCs is less than 1 V because of the high temperature, but the reaction overpotentials are

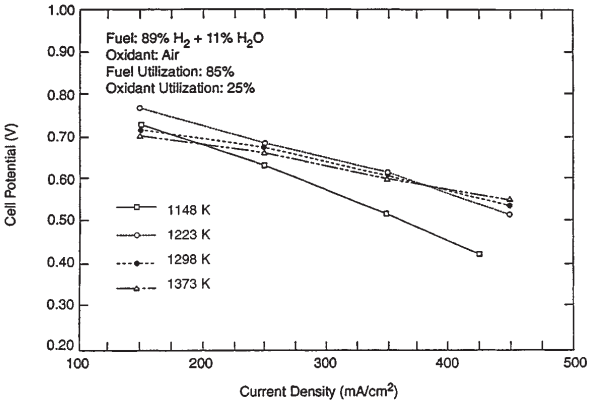


FIG. 27-67 Polarization curves at different temperatures for 50-cm active length thin-wall SOFCs.

small, yielding almost linear curves with slopes corresponding to the resistance of the components.

SOFCs can have a planar geometry similar to PEFCs, but the leading technology is tubular, as shown in Fig. 27-68. The advantage of the tubular arrangement is the absence of high-temperature seals.

Like MCFCs, SOFCs can integrate fuel reforming within the fuel cell stack. A prereformer converts a substantial amount of the natural gas using waste heat from the fuel cell. Compounds containing sulfur (e.g., thiophene, which is commonly added to natural gas as an odorant) must be removed before the reformer. Typically, a hydrodesulfurizer combined with a zinc oxide absorber is used.

The desulfurized natural gas is mixed with the recycled depleted fuel stream containing steam formed in the fuel cell. About 75 percent of the methane is converted to hydrogen and carbon monoxide in the prereformer. The hydrogen-rich fuel is then passed over the fuel cell anode, where 85 percent is converted to electricity. The balance is burned with depleted air in the combustion zone.

The hot combustion gas preheats the fresh air and the prereformer, and can be used further to generate steam. The system is cooled with 200 to 300 percent excess air. A 25-kW SOFC generator system is shown in Fig. 27-69.

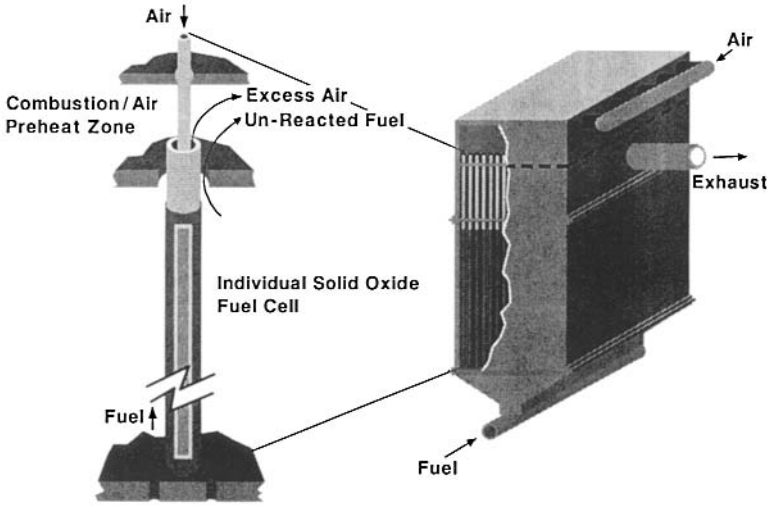


FIG. 27-68 Configuration of the tubular SOFC. (*Courtesy of Westinghouse Electric Corporation.*)

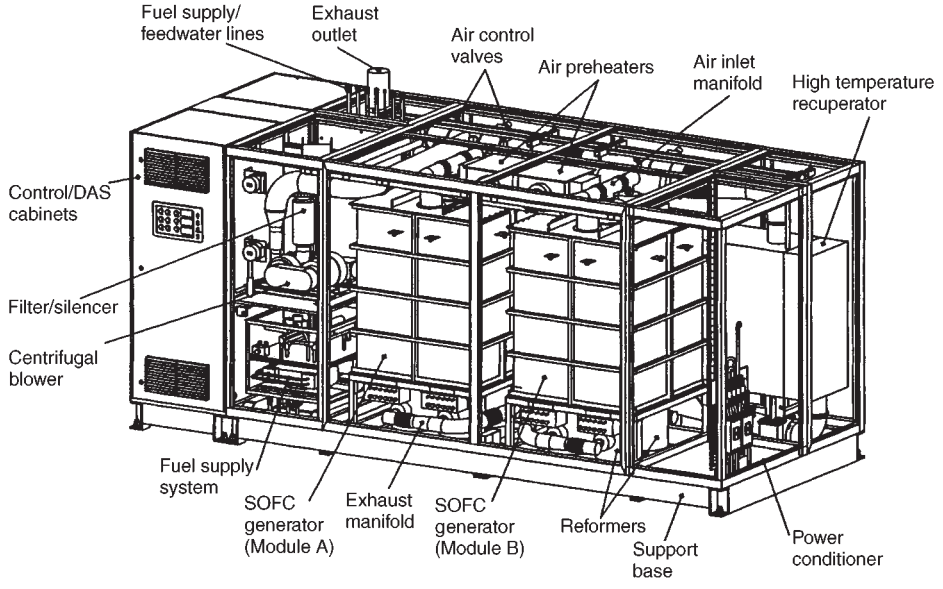


FIG. 27-69 SOFC 25-kW system package. (*Courtesy of Westinghouse Electric Corporation.*)

Materials of Construction*

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* The contributions of R. B. Norton to material used from the fifth edition and of A. S. Krisher and O. W. Siebert to material used from the sixth edition are acknowledged.

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CORROSION AND ITS CONTROL

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INTRODUCTION*

Corrosion is not a favorite subject of engineers. Many a proud designer or project engineer has developed a new component or process with outstanding performance only to have it fail prematurely because of corrosion. Furthermore, despite active research by corrosion engineers, a visit to the local scrap yard shows that large percentages of cars and domestic appliances still fail because of corrosion; this loss pales by comparison when industrial corrosion failures are included. As a result, the annual cost of corrosion and corrosion protection in the United States is on the order of $300 billion, far more than the annual budgets of some small countries.

One of the principal reasons for failure due to reaction with the service environment is the relatively complex nature of the reactions involved. Yet, in spite of all the complex corrosion jargon, whether a metal corrodes depends on the simple electrochemical cell set up by the environment. This might give the erroneous impression that it is possible to calculate such things as the corrosion rate of a car fender in the spring mush of salted city streets. Dr. M. Pourbaix has done some excellent work in the application of thermodynamics to corrosion, but this cannot yet be applied directly to the average complex situation.

Yet, corrosion engineering and science is no longer an empirical art; dissecting a large corrosion problem into its basic mechanisms allows the use of quite sophisticated electrochemical techniques to accomplish satisfactory results. On that positive side, there is real satisfaction and economic gain in designing a component that can resist punishing service conditions under which other parts fail. In some cases, we cannot completely prevent corrosion, but we can try to avoid obsolescence of the component due to corrosion.

FLUID CORROSION

In the selection of materials of construction for a particular fluid system, it is important first to take into consideration the **characteristics of the system,** giving special attention to all factors that may influence corrosion. Since these factors would be peculiar to a particular system, it is impractical to attempt to offer a set of hard and fast rules that would cover all situations.

The **materials** from which the system is to be fabricated are the second important consideration; therefore, knowledge of the characteristics and general behavior of materials when exposed to certain environments is essential.

In the absence of factual corrosion information for a particular set of fluid conditions, a reasonably good selection would be possible from data based on the resistance of materials to a very similar environment. These data, however, should be used with some reservations. Good practice calls for applying such data for preliminary screening. Materials selected thereby would require further study in the fluid system under consideration.

FLUID CORROSION: GENERAL

Metallic Materials Pure metals and their alloys tend to enter into **chemical** union with the elements of a corrosive medium to form stable compounds similar to those found in nature. When metal loss occurs in this way, the compound formed is referred to as the **corrosion product** and the metal surface is spoken of as being **corroded.**

Corrosion is a complex phenomenon that may take any one or more of several forms. It is usually confined to the metal surface, and this is called **general corrosion.** But it sometimes occurs along grain boundaries or other lines of weakness because of a difference in resistance to attack or local electrolytic action.

In most aqueous systems, the corrosion reaction is divided into an anodic portion and a cathodic portion, occurring simultaneously at discrete points on metallic surfaces. Flow of electricity from the anodic to the cathodic areas may be generated by local cells set up either on a single metallic surface (because of local point-to-point differences on the surface) or between dissimilar metals.

Nonmetallics As stated, corrosion of metals applies specifically to chemical or electrochemical attack. The deterioration of plastics and other nonmetallic materials, which are susceptible to swelling, crazing, cracking, softening, and so on, is essentially **physiochemical** rather than electrochemical in nature. Nonmetallic materials can either be rapidly deteriorated when exposed to a particular environment or, at the other extreme, be practically unaffected. Under some conditions, a nonmetallic may show evidence of gradual deterioration. However, it is seldom possible to evaluate its chemical resistance by measurements of weight loss alone, as is most generally done for metals.

FLUID CORROSION: LOCALIZED

Pitting Corrosion Pitting is a form of corrosion that develops in highly localized areas on the metal surface. This results in the development of cavities or pits. They may range from deep cavities of small diameter to relatively shallow depressions. Pitting examples: aluminum and stainless alloys in aqueous solutions containing chloride. **Inhibitors** are sometimes helpful in preventing pitting.

Crevice Corrosion Crevice corrosion occurs within or adjacent to a crevice formed by contact with another piece of the same or another metal or with a nonmetallic material. When this occurs, the intensity of attack is usually more severe than on surrounding areas of the same surface.

This form of corrosion can result because of a deficiency of oxygen in the crevice, acidity changes in the crevice, buildup of ions in the crevice, or depletion of an inhibitor.

* Abstracted from texts by Flinn and Trojan, with permission of John Wiley & Sons.

Oxygen-Concentration Cell The oxygen-concentration cell is an electrolytic cell in which the driving force to cause corrosion results from a difference in the amount of oxygen in solution at one point as compared with another. Corrosion is accelerated where the oxygen concentration is least, for example, in a stuffing box or under gaskets. This form of corrosion will also occur under solid substances that may be deposited on a metal surface and thus shield it from ready access to oxygen. Redesign or change in mechanical conditions must be used to overcome this situation.

Galvanic Corrosion Galvanic corrosion is the corrosion rate above normal that is associated with the flow of current to a less active metal (cathode) in contact with a more active metal (anode) in the same environment. Tables 28-1*a* and 28-1*b* show the **galvanic** series of various metals. It should be used with caution, since exceptions to this series in actual use are possible. However, as a general rule, when dissimilar metals are used in contact with each other and are exposed to an electrically conducting solution, combinations of metals that are as close as possible in the galvanic series should be chosen. Coupling two metals widely separated in this series generally will produce accelerated attack on the more active metal. Often, however, protective oxide films and other effects will tend to reduce galvanic corrosion. Galvanic corrosion can, of course, be prevented by **insulating** the metals from each other. For example, when plates are bolted together, specially designed plastic washers can be used.

Potential differences leading to galvanic-type cells can also be set up on a single metal by differences in temperature, velocity, or concentration (see subsection "Crevice Corrosion").

Area effects in galvanic corrosion are very important. An unfavorable area ratio is a large cathode and a small anode. Corrosion of the anode may be 100 to 1,000 times greater than if the two areas were the same. This is the reason why stainless steels are susceptible to rapid pitting in some environments. Steel rivets in a copper plate will corrode much more severely than a steel plate with copper rivets.

Intergranular Corrosion Selective corrosion in the grain boundaries of a metal or alloy without appreciable attack on the grains or crystals themselves is called intergranular corrosion. When severe, this attack causes a loss of strength and ductility out of proportion to the amount of metal actually destroyed by corrosion.

The **austenitic stainless steels** that are not stabilized or that are not of the extra-low-carbon types, when heated in the temperature range of 450 to 843°C (850 to 1,550°F), have chromium-rich compounds (chromium carbides) precipitated in the grain boundaries. This causes grain-boundary impoverishment of chromium and makes the affected metal susceptible to intergranular corrosion in many environments. Hot nitric acid is one environment which causes severe intergranular corrosion of austenitic stainless steels with grain-boundary precipitation. Austenitic stainless steels stabilized with niobium (columbium) or titanium to decrease carbide formation or containing less than 0.03 percent carbon are normally not susceptible to grain-boundary deterioration when heated in the given temperature range. Unstabilized austenitic stainless steels or types with normal carbon content, to be immune to intergranular corrosion, should be given a solution anneal. This consists of heating to 1,090°C (2,000°F), holding at this temperature for a minimum of 1 h/in of thickness, followed by rapidly quenching in water (or, if impractical because of large size, rapidly cooling with an air-water spray).

Stress-Corrosion Cracking Corrosion can be accelerated by stress, either residual internal stress in the metal or externally applied stress. Residual stresses are produced by deformation during fabrication, by unequal cooling from high temperature, and by internal structural rearrangements involving volume change. Stresses induced by rivets and bolts and by press and shrink fits can also be classified as residual stresses. Tensile stresses at the surface, usually of a magnitude equal to the yield stress, are necessary to produce stress-corrosion cracking. However, failures of this kind have been known to occur at lower stresses.

Virtually every alloy system has its specific environment conditions which will produce stress-corrosion cracking, and the time of exposure required to produce failure will vary from minutes to years. Typical examples include cracking of cold-formed brass in ammonia environments, cracking of austenitic stainless steels in the presence of chlorides, cracking of Monel in hydrofluosilicic acid, and caustic embrittlement cracking of steel in caustic solutions.

This form of corrosion can be prevented in some instances by eliminating high stresses. Stresses developed during fabrication, particularly during welding, are frequently the main source of trouble. Of course, temperature and concentration are also important factors in this type of attack.

Presence of **chlorides** does not generally cause cracking of austenitic stainless steels when temperatures are below about 50°C (120°F). However, when temperatures are high enough to concentrate chlorides on the stainless surface, cracking may occur when the chloride concentration in the surrounding media is a few parts per million. Typical examples are cracking of heat-exchanger tubes at the crevices in rolled joints and under scale formed in the vapor space below the top tube sheet in vertical heat exchangers. The cracking of

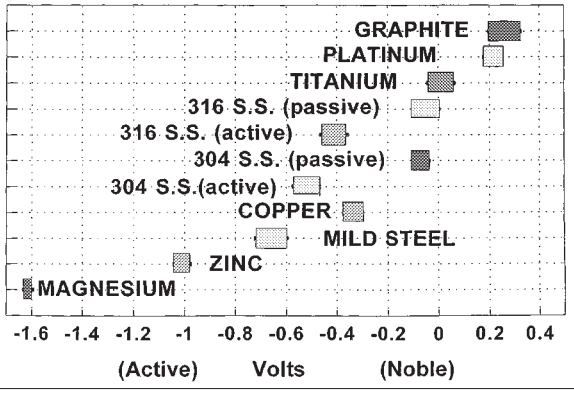
TABLE 28-1*a* Galvanic Series of Metals and Alloys

Corroded end (anodic, or least noble)

Magnesium
Magnesium alloys
Zinc
Aluminum alloys
Aluminum
Alclad
Cadmium
Mild steel
Cast iron
Ni-Resist
13% chromium stainless (active)
50-50 lead-tin solder
18-8 stainless type 304 (active)
18-8-3 stainless type 316 (active)
Lead
Tin
Muntz Metal
Naval brass
Nickel (active)
Inconel 600 (active)
Yellow brass
Admiralty brass
Aluminum bronze
Red brass
Copper
Silicon bronze
70-30 cupronickel
Nickel (passive)
Inconel 600 (passive)
Monel 400
18-8 stainless type 304 (passive)
18-8-3 stainless type 316 (passive)
Silver
Graphite
Gold
Platinum

Protected end (cathodic, or most noble)

TABLE 28-1*b* Galvanic Series in Sea Water (Approx.), Volts vs. Sat. Calomel Ref. Electrode



stainless steel under insulation is caused when chloride-containing water is concentrated on the hot surfaces. The chlorides may be leached from the insulation or may be present in the water when it enters the insulation. Improved design and maintenance of insulation weatherproofing, coating of the metal prior to the installation of insulation, and use of chloride-free insulation are all steps which will help to reduce (but not eliminate) this problem.

Serious stress-corrosion-cracking failures have occurred when chloride-containing hydrotest water was not promptly removed from stainless-steel systems. Use of potable-quality water and complete draining after test comprise the most reliable solution to this problem. Use of chloride-free water is also helpful, especially when prompt drainage is not feasible.

In handling caustic, as-welded steel can be used without developing caustic-embrittlement cracking if the temperature is below 50°C (120°F). If the temperature is higher and particularly if the concentration is above about 30 percent, cracking at and adjacent to non-stress-relieved welds frequently occurs.

Liquid-Metal Corrosion Liquid metals can also cause corrosion failures. The most damaging are liquid metals which penetrate the metal along grain boundaries to cause catastrophic failure. Examples include mercury attack on aluminum alloys and attack of stainless steels by molten zinc or aluminum. A fairly common problem occurs when galvanized-structural-steel attachments are welded to stainless piping or equipment. In such cases it is mandatory to remove the galvanizing completely from the area which will be heated above 260°C (500°F).

Erosion Erosion is the destruction of a metal by abrasion or attrition caused by the flow of liquid or gas (with or without suspended solids). The use of harder materials and changes in velocity or environment are methods employed to prevent erosion attack.

Impingement Corrosion This phenomenon is sometimes referred to as erosion-corrosion or velocity-accelerated corrosion. It occurs when damage is accelerated by the mechanical removal of corrosion products (such as oxides) which would otherwise tend to stifle the corrosion reaction.

Corrosion Fatigue Corrosion fatigue is a reduction by corrosion of the ability of a metal to withstand **cyclic or repeated stresses.** The surface of the metal plays an important role in this form of damage, as it will be the most highly stressed and at the same time subject to attack by the corrosive media. Corrosion of the metal surface will lower fatigue resistance, and stressing of the surface will tend to accelerate corrosion.

Under cyclic or repeated stress conditions, rupture of protective oxide films that prevent corrosion takes place at a greater rate than that at which new protective films can be formed. Such a situation frequently results in formation of anodic areas at the points of rupture; these produce pits that serve as stress-concentration points for the origin of cracks that cause ultimate failure.

Cavitation Formation of transient voids or vacuum bubbles in a liquid stream passing over a surface is called cavitation. This is often encountered around propellers, rudders, and struts and in pumps. When these bubbles collapse on a metal surface, there is a severe impact or explosive effect that can cause considerable mechanical damage, and corrosion can be greatly accelerated because of the destruction of protective films. Redesign or a more resistant metal is generally required to avoid this problem.

Fretting Corrosion This attack occurs when metals slide over each other and cause mechanical damage to one or both. In such a case, frictional heat oxidizes the metal and this oxide then wears away; or the mechanical removal of protective oxides results in exposure of fresh surface for corrosive attack. Fretting corrosion is minimized by using harder materials, minimizing friction (via lubrication), or designing equipment so that no relative movement of parts takes place.

Hydrogen Attack At elevated temperatures and significant hydrogen partial pressures, hydrogen will penetrate carbon steel, reacting with the carbon in the steel to form methane. The pressure generated causes a loss of ductility (hydrogen embrittlement) and failure by cracking or blistering of the steel. The removal of the carbon from the steel (decarburization) results in decreased strength. Resistance to this type of attack is improved by alloying with molybdenum or chromium. Accepted limits for the use of carbon and low-alloy steels are shown in Fig. 28-1, which is adapted from American Petroleum Institute (API) Publication 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants,* the so-called Nelson curves.

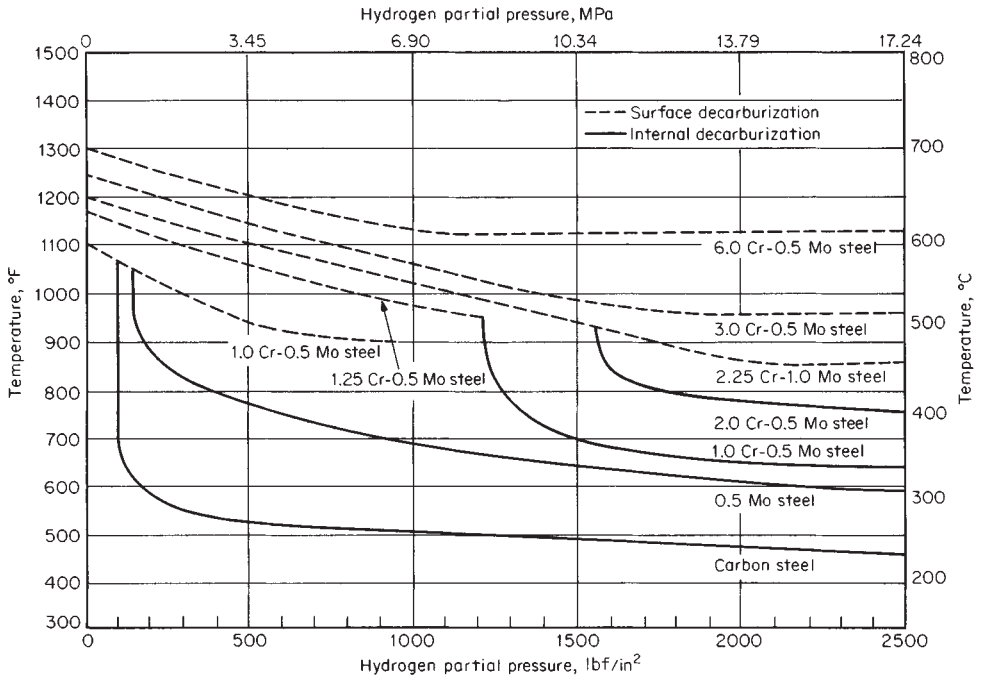


FIG. 28-1 Operating limits for steels in hydrogen service. Each steel is suitable for use under hydrogen-partial-pressure-temperature conditions below and to the left of its respective curve. (*Courtesy of National Association of Corrosion Engineers.*)

Hydrogen damage can also result from hydrogen generated in electrochemical corrosion reactions. This phenomenon is most commonly observed in solutions of specific weak acids. H_2S and HCN are the most common, although other acids can cause the problem. The atomic hydrogen formed on the metal surface by the corrosion reaction diffuses into the metal and forms molecular hydrogen at microvoids in the metal. The result is failure by embrittlement, cracking, and blistering.

FLUID CORROSION: STRUCTURAL

Graphitic Corrosion Graphitic corrosion usually involves **gray cast iron** in which metallic iron is converted into corrosion products, leaving a residue of intact graphite mixed with iron-corrosion products and other insoluble constituents of cast iron.

When the layer of graphite and corrosion products is impervious to the solution, corrosion will cease or slow down. If the layer is porous, corrosion will progress by galvanic behavior between graphite and iron. The rate of this attack will be approximately that for the maximum penetration of steel by pitting. The layer of graphite formed may also be effective in reducing the galvanic action between cast iron and more noble alloys such as bronze used for valve trim and impellers in pumps.

Low-alloy cast irons frequently demonstrate a superior resistance to graphitic corrosion, apparently because of their denser structure and the development of more compact and more protective graphitic coatings. Highly alloyed **austenitic cast irons** show considerable superiority over gray cast irons to graphitic corrosion because of the more noble potential of the austenitic matrix plus more protective graphitic coatings.

Carbon steels heated for prolonged periods at temperatures above 455°C (850°F) may be subject to the segregation of carbon, which is transformed into graphite. When this occurs, the structural strength of the steel will be affected. Killed steels or low-alloy steels of chromium and molybdenum or chromium and nickel should be considered for elevated-temperature services.

Parting, or Dealloying, Corrosion This type of corrosion occurs when only one component of an alloy is removed by corrosion. The most common type is dezincification of brass.

Dezincification Dezincification is corrosion of a brass alloy containing zinc in which the principal product of corrosion is metallic copper. This may occur as plugs filling pits (plug type) or as continuous layers surrounding an unattacked core of brass (general type). The mechanism may involve overall corrosion of the alloy followed by redeposition of the copper from the corrosion products or selective corrosion of zinc or a high-zinc phase to leave copper residue. This form of corrosion is commonly encountered in brasses that contain more than 15 percent zinc and can be either eliminated or reduced by the addition of small amounts of **arsenic, antimony,** or **phosphorus** to the alloy.

Biological Corrosion The metabolic activity of microorganisms can either directly or indirectly cause deterioration of a metal by corrosion processes. Such activity can (1) produce a corrosive environment, (2) create electrolytic-concentration cells on the metal surface, (3) alter the resistance of surface films, (4) have an influence on the rate of anodic or cathodic reaction, and (5) alter the environment composition.

Microorganisms associated with corrosion are of two types, aerobic and anaerobic. **Aerobic** microorganisms readily grow in an environment containing oxygen, while the **anaerobic** species thrive in an environment virtually devoid of atmospheric oxygen.

The manner in which many of these bacteria carry on their chemical processes is quite complicated and in some cases not fully understood. The role of **sulfate-reducing bacteria** (anaerobic) in promoting corrosion has been extensively investigated. The sulfates in slightly acid to alkaline (pH 6 to 9) soils are reduced by these bacteria to form calcium sulfide and hydrogen sulfide. When these compounds come in contact with underground iron pipes, conversion of the iron to iron sulfide occurs. As these bacteria thrive under these conditions, they will continue to promote this reaction until failure of the pipe occurs.

Several instances of serious biological corrosion occurred when hydrotest water was not promptly removed from stainless-steel systems. These cases involved both potable and nonpotable waters. Biological activity caused perforation of the stainless steel in a few months. Use of potable-quality water and prompt and complete draining after a test constitute the most reliable solution to this problem.

Microbiologically Influenced Corrosion (MIC)* While microbiologically influenced corrosion has existed since the beginning of time, it has only been identified to be a real and persistent problem to industry during the past several decades. A considerable amount of multidisciplinary effort has been expended to determine the extent of the problem and to understand the phenomenon. Prevention and control would seem to be a product of this understanding. Unfortunately, the more we learn, the more we find out how little we really understand about the subject. MIC is now recognized as a problem in many industries, including the gas pipeline, nuclear and fossil power, chemical process, and pulp and paper industries. This brief review is presented from an industrial point of view. Subjects include the buried structures, materials selection, hydrotest procedures, and other considerations that corrosion engineers in the field need to take into account in order to prevent or minimize potential MIC problems in the future.

It is widely recognized that microorganisms attach to, form films on, and influence the corrosion of metals and alloys immersed in natural aqueous environments. The microorganisms influence corrosion by changing the electrochemical conditions at the metal surface. Theoretically, these changes may have many effects, ranging from the induction of localized corrosion, to a change in the rate of general corrosion, to corrosion inhibition. In every case, however, the process of corrosion is electrochemical.

Recently, there has developed a greater recognition of the complexity of the MIC process. MIC is rarely linked to a unique mechanism or to a single species of microorganisms. At the present state of knowledge, it is widely accepted that the growth of different microbial species within adherent biofilms facilitates the development of structured consortia that may enhance the microbial effects on corrosion.

Most practicing engineers are not, and do not need to become, experts in the details of MIC. What is needed is to recognize that this corrosion system is active, that process equipment and structures are at risk, and that there are numerous tools available to monitor and detect MIC (see the later sections on laboratory and field corrosion testing, both of which address the subject of MIC). Advances in the detection of MIC have been made principally through education in the methods for proper observation of field samples, sample collection, cultivation of bacteria involved, microscopic analysis of samples, and metallurgical analysis of samples. These have greatly improved our ability to *prove* the involvement of microbes in the corrosion processes. Recent techniques developed in the laboratory make use of specific antibodies directed against organisms known to be MIC-causing organisms, give rapid and quantitative answers to questions regarding the numbers and types of microbes present in field samples, and can be used in the field.

Bacteria, as a group, can grow over a pH range of about 0 to 11. They can be obligate aerobes (require oxygen to survive and grow), microaerophiles (require low oxygen concentrations), facultative anaerobes (prefer aerobic conditions but will live under anaerobic conditions), or obligate anaerobes (will grow only under conditions where oxygen is absent). It should be emphasized that most anaerobes will survive aerobic conditions for quite a while and the same is true for aerobes in anaerobic conditions. Also note that, for a microorganism, anaerobic conditions may be quite easily found in what are thought to be generally aerobic environments. Often these anaerobic microenvironments are in, or under, films, in particulates of debris, inside crevices, and so on.

As a group, the MIC-causing bacteria may use almost any available organic carbon molecules, from simple alcohols or sugars to phenols to wood or various other complex polymers as food (heterotrophs), or they may fix CO_2 (autotropha) as do plants. Some use inorganic elements or ions (e.g., NH or NO, CH, H, S, Fe, Mn, etc.), as sources of

* Excerpted from papers by John G. Stoecker II and Oliver W. Siebert, courtesy of NACE International.

energy. The nutritional requirements of these organisms, therefore, range from very simple to very complex. Most fall in between these extremes and require a limited number of organic molecules, moderate temperatures, moist environments, and near-neutral pH.

Buried Structures Corrosion of buried pipelines caused by sulfate-reducing bacteria has been studied for almost a century. Quite by accident, industry has been protecting buried iron-based structures from bacterial damage through the use of cathodic protection. Cathodic protection produces an elevated alkaline or basic environment on the surface of the buried structure (pH ≥10) which is not conducive to microbiological growth. Booth was one of the early investigators to present this finding, but caution should be exercised when using his recommendations. The user of cathodic protection must also consider the material being protected with regard to caustic cracking; a cathodic potential driven to the negative extreme of –0.95 V for microbiological protection purposes can cause caustic cracking of a steel structure. The benefits and risks of cathodic protection must be weighed for each material and each application.

There has been no dramatic improvement in the microbiological protection of buried structures over the years. Cathodic protection in conjunction with a protective coating system has continued to be the best defense against this form of MIC as well as against other underground corrosive damage. Cathodic protection provides caustic-environment protection at the holes or holidays in the coating that are sure to develop with time due to one cause or another. Experience has been that coating systems, by themselves, do not provide adequate protection for a buried structure over the years; for best results, a properly designed and maintained cathodic protection system *must* be used in conjunction with a protective coating (regardless of the quality of the coating, as applied).

Backfilling with limestone or other alkaline material is an added step to protect buried structures from microbiological damage. Providing adequate drainage to produce a dry environment both above and below ground in the area of the buried structure will also reduce the risk of this type of damage.

Waters While MIC-causing bacteria may arrive at the surface of their corrosion worksite by almost any transportation system, there is always water present to allow them to become active and cause MIC to occur. There are plenty of examples of even superpure waters having sufficient microorganisms present to feed, divide, and multiply when even the smallest trace of a viable food-stuff is present (e.g., the so-called *water for injection* in the pharmaceutical industry has been the observed subject of extensive corrosion of polished stainless steel tanks, piping, and so on).

The initial MIC examples studied in the 1970s were weld failures of stainless steel piping that saw only potable drinking water. The numbers of water-exposed systems that have been verified as being affected by MIC are legion.

Hydrostatic Testing Waters Microbiological species in the water used for hydrostatic (safety) testing of process equipment and for process batch water have caused considerable MIC damage and expense in the past. Guidelines for hydrotesting have been adopted by several industrial and governmental organizations in an effort to prevent this damage. Generally, good results have been reported for those who have followed this practice. Unfortunately, this can be a *very* expensive undertaking where the need cannot be totally quantified (and, thus, justified to management). Cost-cutting practices which either ignore these guides or follow an adulteration of proven precautions can lead to major MIC damage to equipment and process facilities.

Obviously, natural freshwater from wells, lakes, or rivers is the least desirable and its use should be avoided. Even potable waters are not free of organic species that cause MIC damage to conventional materials of construction; for example, steel, stainless steels, and so on. If the size of the facility argues strongly against the use of demineralized water or steam condensate, potable water must be evaluated for test use. Perhaps it would be possible to use a biocide such as hydrogen peroxide or ozone in the potable water; most organic biocides cause disposal problems. Obviously, chlorine must be used only with great care because of the extensive damage it will cause to the 300-series, austenitic stainless steels. In all cases, as soon as the test is over, the water *must* be *completely* drained and the system thoroughly dried so that no vestiges of water are allowed to be trapped in occluded areas.

The literature abounds with instructions as to the proper manner in which to accomplish the necessary and MIC-safe testing procedures. The engineering personnel planning these test operations should avail themselves of that knowledge.

Materials of Construction MIC is a process in which manufactured materials deteriorate through microbiological action. This process can be either direct or indirect.

Microbial biodeterioration of a great many materials (including concretes, glasses, metals and their alloys, and plastics) occurs by diverse mechanisms.

The corrosion engineers' solution to corrosion problems sometimes includes an upgrading of the materials of construction. This is a natural approach, and since microbiological corrosion has usually been considered a form of crevice or under-deposit attack, this option is logical. Unfortunately, with MIC, the use of more corrosion-resistant materials can many times be a shortcut to disaster; MIC is dependent upon the species of organism involved. As an example, an upgrade from type 304 to 316 stainless steel does not always help. Kobrin reported biological corrosion of delta ferrite stringers in weld metal. Obviously, this upgrade was futile; type 316 stainless steel can contain as much or more delta ferrite as does type 304. Kobrin also reported MIC of nickel, nickel-copper Alloy 400, and nickel-molybdenum Alloy B heat exchanger tubes. Although the Alloy 400 and Alloy B were not pitted as severely as the nickel tubes, the higher alloys did not solve the corrosion problem.

In the past, copper was believed to be toxic to *most* microbiological species. This has not turned out to be the case, as pointed out in the preceding example, reported in many other studies by the authors and their colleagues. As an example, reports from engineers in the power generating industry about MIC of copper and cupro-nickel alloys also indicate that copper is not an automatic deterrent to this corrosion mechanism. It is concluded that copper is toxic to the higher life-forms, for example, barnacles and so on, but it is not a biocide to the simple, single-cell organisms.

At this stage of knowledge about MIC, only titanium, zirconium, and tantalum appear to be immune to microbiological damage.

FACTORS INFLUENCING CORROSION

Solution pH The corrosion rate of most metals is affected by pH. The relationship tends to follow one of three general patterns:

1. Acid-soluble metals such as iron have a relationship as shown in Fig. 28-2*a*. In the middle pH range (≈4 to 10), the corrosion rate is controlled by the rate of transport of oxidizer (usually dissolved O_2) to the metal surface. Iron is weakly amphoteric. At very high temperatures such as those encountered in boilers, the corrosion rate increases with increasing basicity, as shown by the dashed line.
2. Amphoteric metals such as aluminum and zinc have a relationship as shown in Fig. 28-2*b*. These metals dissolve rapidly in either acidic or basic solutions.
3. Noble metals such as gold and platinum are not appreciably affected by pH, as shown in Fig. 28-2*c*.

Oxidizing Agents In some corrosion processes, such as the solution of zinc in hydrochloric acid, hydrogen may evolve as a gas. In others, such as the relatively slow solution of copper in sodium chloride, the removal of hydrogen, which must occur so that corrosion may proceed, is effected by a reaction between hydrogen and some oxidizing chemical such as oxygen to form water. Because of the high rates of corrosion which usually accompany hydrogen evolution, metals are rarely used in solutions from which they evolve hydrogen at an appreciable rate. As a result, most of the corrosion observed in practice occurs under conditions in which the oxidation of hydrogen to form water is a necessary part of the corrosion process. For this reason, oxidizing agents are often powerful accelerators of corrosion, and in many cases the **oxidizing power of a solution** is its most important single property insofar as corrosion is concerned.

Oxidizing agents that accelerate the corrosion of some materials may also retard corrosion of others through the formation on their surface of oxides or layers of adsorbed oxygen which make them more

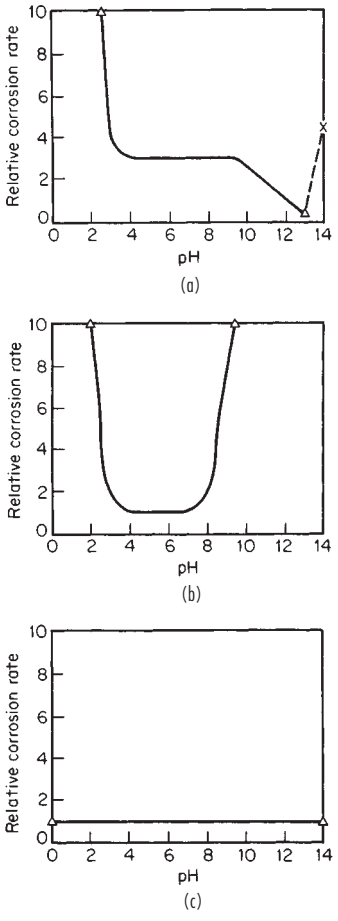


FIG. 28-2 Effect of pH on the corrosion rate. (*a*) Iron. (*b*) Amphoteric metals (aluminum, zinc). (*c*) Noble metals.

resistant to chemical attack. This property of chromium is responsible for the principal corrosion-resisting characteristics of the stainless steels.

It follows, then, that oxidizing substances, such as dissolved air, may accelerate the corrosion of one class of materials and retard the corrosion of another class. In the latter case, the behavior of the material usually represents a balance between the power of oxidizing compounds to preserve a protective film and their tendency to accelerate corrosion when the agencies responsible for protective-film breakdown are able to destroy the films.

Temperature The rate of corrosion tends to increase with rising temperature. Temperature also has a secondary effect through its influence on the solubility of air (oxygen), which is the most common oxidizing substance influencing corrosion. In addition, temperature has specific effects when a temperature change causes phase changes which introduce a corrosive second phase. Examples include condensation systems and systems involving organics saturated with water.

Velocity An increase in the velocity of relative movement between a corrosive solution and a metallic surface frequently tends to accelerate corrosion. This effect is due to the higher rate at which the corrosive chemicals, including oxidizing substances (air), are brought to the corroding surface and to the higher rate at which corrosion products, which might otherwise accumulate and stifle corrosion, are carried away. The higher the velocity, the thinner will be the films which corroding substances must penetrate and through which soluble corrosion products must diffuse.

Whenever corrosion resistance results from the accumulation of layers of insoluble corrosion products on the metallic surface, the effect of high velocity may be either to prevent their normal formation or to remove them after they have been formed. Either effect allows corrosion to proceed unhindered. This occurs frequently in small-diameter tubes or pipes through which corrosive liquids may be circulated at high velocities (e.g., condenser and evaporator tubes), in the vicinity of bends in pipe lines, and on propellers, agitators, and centrifugal pumps. Similar effects are associated with cavitation and impingement corrosion.

Films Once corrosion has started, its further progress very often is controlled by the nature of films, such as passive films, that may form or accumulate on the metallic surface. The classical example is the thin **oxide film** that forms on stainless steels.

Insoluble corrosion products may be completely impervious to the corroding liquid and, therefore, completely protective; or they may be quite permeable and allow local or general corrosion to proceed unhindered. Films that are nonuniform or discontinuous may tend to localize corrosion in particular areas or to induce accelerated corrosion at certain points by initiating electrolytic effects of the concentration-cell type. Films may tend to retain or absorb moisture and thus, by delaying the time of drying, increase the extent of corrosion resulting from exposure to the atmosphere or to corrosive vapors.

It is agreed generally that the characteristics of the **rust films** that form on steels determine their resistance to atmospheric corrosion. The rust films that form on low-alloy steels are more protective than those that form on unalloyed steel.

In addition to films that originate at least in part in the corroding metal, there are others that originate in the corrosive solution. These include various salts, such as carbonates and sulfates, which may be precipitated from heated solutions, and insoluble compounds, such as "beer stone," which form on metal surfaces in contact with certain specific products. In addition, there are films of oil and grease that may protect a material from direct contact with corrosive substances. Such oil films may be applied intentionally or may occur naturally, as in the case of metals submerged in sewage or equipment used for the processing of oily substances.

Other Effects Stream **concentration** can have important effects on corrosion rates. Unfortunately, corrosion rates are seldom linear with concentration over wide ranges. In equipment such as distillation columns, reactors, and evaporators, concentration can change continuously, making prediction of corrosion rates rather difficult. Concentration is important during plant shutdown; presence of moisture that collects during cooling can turn innocuous chemicals into dangerous corrosives.

As to the effect of time, there is no universal law that governs the reaction for all metals. Some corrosion rates remain constant with time over wide ranges, others slow down with time, and some alloys have increased corrosion rates with respect to time. Situations in which the corrosion rate follows a combination of these paths can develop. Therefore, extrapolation of corrosion data and corrosion rates should be done with utmost caution.

Impurities in a corrodent can be good or bad from a corrosion standpoint. An impurity in a stream may act as an inhibitor and actually retard corrosion. However, if this impurity is removed by some process change or improvement, a marked rise in corrosion rates can result. Other impurities, of course, can have very deleterious effects on materials. The chloride ion is a good example; small amounts of chlorides in a process stream can break down the passive oxide film on stainless steels. The effects of impurities are varied and complex. One must be aware of what they are, how much is present, and where they come from before attempting to recommend a particular material of construction.

HIGH-TEMPERATURE ATTACK

Physical Properties The suitability of an alloy for high-temperature service [425 to 1,100°C (800 to 2,000°F)] is dependent upon properties inherent in the alloy composition and upon the conditions of application. Crystal structure, density, thermal conductivity, electrical resistivity, thermal expansivity, structural stability, melting

range, and vapor pressure are all physical properties basic to and inherent in individual alloy compositions.

Of usually high relative importance in this group of properties is **expansivity.** A surprisingly large number of metal failures at elevated temperatures are the result of excessive thermal stresses originating from constraint of the metal during heating or cooling. Such constraint in the case of hindered contraction can cause rupturing.

Another important property is alloy **structural stability.** This means freedom from formation of new phases or drastic rearrangement of those originally present within the metal structure as a result of thermal experience. Such changes may have a detrimental effect upon strength or corrosion resistance or both.

Mechanical Properties Mechanical properties of wide interest include creep, rupture, short-time strengths, and various forms of ductility, as well as resistance to impact and fatigue stresses. Creep strength and stress rupture are usually of greatest interest to designers of stationary equipment such as vessels and furnaces.

Corrosion Resistance Possibly of greater importance than physical and mechanical properties is the ability of an alloy's chemical composition to resist the corrosive action of various hot environments. The forms of high-temperature corrosion which have received the greatest attention are **oxidation** and **scaling.**

Chromium is an essential constituent in alloys to be used above 550°C (1,000°F). It provides a tightly adherent oxide film that materially retards the oxidation process. Silicon is a useful element in imparting oxidation resistance to steel. It will enhance the beneficial effects of chromium. Also, for a given level of chromium, experience has shown oxidation resistance to improve as the nickel content increases.

Aluminum is not commonly used as an alloying element in steel to improve oxidation resistance, as the amount required interferes with both workability and high-temperature-strength properties. However, the development of high-aluminum surface layers by various methods, including spraying, cementation, and dipping, is a feasible means of improving heat resistance of low-alloy steels.

Contaminants in fuels, especially alkali-metal ions, vanadium, and sulfur compounds, tend to react in the combustion zone to form molten fluxes which dissolve the protective oxide film on stainless steels, allowing oxidation to proceed at a rapid rate. This problem is becoming more common as the high cost and short supply of natural gas and distillate fuel oils force increased usage of residual fuel oils and coal.

COMBATING CORROSION

Material Selection The objective is to select the material which will most economically fulfill the process requirements. The best source of data is well-documented experience in an identical process unit. In the absence of such data, other data sources such as experience in pilot units, corrosion-coupon tests in pilot or bench-scale units, laboratory corrosion-coupon tests in actual process fluids, or corrosion-coupon tests in synthetic solutions must be used. The data from such alternative sources (which are listed in decreasing order of reliability) must be properly evaluated, taking into account the degree to which a given test may fail to reproduce actual conditions in an operating unit. Particular emphasis must be placed on possible composition differences between a static laboratory test and a dynamic plant as well as on trace impurities (chlorides in stainless-steel systems, for example) which may greatly change the corrosiveness of the system. The possibility of severe localized attack (pitting, crevice corrosion, or stress-corrosion cracking) must also be considered.

Permissible **corrosion rates** are an important factor and differ with equipment. Appreciable corrosion can be permitted for tanks and lines if anticipated and allowed for in design thickness, but essentially no corrosion can be permitted in fine-mesh wire screens, orfices, and other items in which small changes in dimensions are critical.

In many instances use of **nonmetallic materials** will prove to be attractive from an economic and performance standpoint. These should be considered when their strength, temperature, and design limitations are satisfactory.

Proper Design Design considerations with respect to minimizing corrosion difficulties should include the desirability for free and complete drainage, minimizing crevices, and ease of cleaning and inspection. The installation of baffles, stiffeners, and drain nozzles and the location of valves and pumps should be made so that free drainage will occur and washing can be accomplished without holdup. Means of access for inspection and maintenance should be provided whenever practical. Butt joints should be used whenever possible. If lap joints employing fillet welds are used, the welds should be continuous.

The use of dissimilar metals in contact with each other should generally be minimized, particularly if they are widely separated in their nominal positions in the galvanic series (see Table 28-1*a*). If they are to be used together, consideration should be given to insulating them from each other or making the anodic material area as large as possible.

Equipment should be supported in such a way that it will not rest in pools of liquid or on damp insulating material. Porous insulation should be weatherproofed or otherwise protected from moisture and spills to avoid contact of the wet material with the equipment. Specifications should be sufficiently comprehensive to ensure that the desired composition or type of material will be used and the right condition of heat treatment and surface finish will be provided. Inspection during fabrication and prior to acceptance is desirable.

Altering the Environment Simple changes in environment may make an appreciable difference in the corrosion of metals and should be considered as a means of combating corrosion. **Oxygen** is an important factor, and its removal or addition may cause marked changes in corrosion. The treatment of boiler feedwater to remove oxygen, for instance, greatly reduces the corrosiveness of the water on steel. Inert-gas purging and blanketing of many solutions, particularly acidic media, generally minimize corrosion of copper and nickel-base alloys by minimizing air or oxygen content. Corrosiveness of acid media to stainless alloys, on the other hand, may be reduced by aeration because of the formation of passive oxide films. Reduction in temperature will almost always be beneficial with respect to reducing corrosion if no corrosive phase changes (condensation, for example) result. Velocity effects vary with the material and the corrosive system. When pH values can be modified, it will generally be beneficial to hold the acid level to a minimum. When acid additions are made in batch processes, it may be beneficial to add them last so as to obtain maximum dilution and minimum acid concentration and exposure time. Alkaline pH values are less critical than acid values with respect to controlling corrosion. Elimination of moisture can and frequently does minimize, if not prevent, corrosion of metals, and this possibility of environmental alteration should always be considered.

Inhibitors The use of various substances or inhibitors as additives to corrosive environments to decrease corrosion of metals in the environment is an important means of combating corrosion. This is generally most attractive in closed or recirculating systems in which the annual cost of inhibitor is low. However, it has also proved to be economically attractive for many once-through systems, such as those encountered in petroleum-processing operations. Inhibitors are effective as the result of their controlling influence on the cathode- or anode-area reactions.

Typical examples of inhibitors used for minimizing corrosion of iron and steel in aqueous solutions are the chromates, phosphates, and silicates. Organic sulfide and amine materials are frequently effective in minimizing corrosion of iron and steel in acid solution.

The use of inhibitors is not limited to controlling corrosion of iron and steel. They frequently are effective with stainless steel and other alloy materials. The addition of copper sulfate to dilute sulfuric acid will sometimes control corrosion of stainless steels in hot dilute solutions of this acid, whereas the uninhibited acid causes rapid corrosion.

The effectiveness of a given inhibitor generally increases with an increase in **concentration,** but inhibitors considered practical and economically attractive are used in quantities of less than 0.1 percent by weight.

In some instances the amount of inhibitor present is critical in that a deficiency may result in localized or pitting attack, with the overall results being more destructive than when none of the inhibitor is present. Considerations for the use of inhibitors should therefore include review of experience in similar systems or investigation of requirements and limitations in new systems.

Cathodic Protection This electrochemical method of corrosion control has found wide application in the protection of carbon steel underground structures such as pipe lines and tanks from external soil corrosion. It is also widely used in water systems to protect ship hulls, offshore structures, and water-storage tanks.

Two methods of providing cathodic protection for minimizing corrosion of metals are in use today. These are the sacrificial-anode method and the impressed-emf method. Both depend upon making the metal to be protected the cathode in the electrolyte involved.

Examples of the sacrificial-anode method include the use of zinc, magnesium, or aluminum as anodes in electrical contact with the metal to be protected. These may be anodes buried in the ground for protection of underground pipe lines or attachments to the surfaces of equipment such as condenser water boxes or on ship hulls. The current required is generated in this method by corrosion of the sacrificial-anode material. In the case of the impressed emf, the direct current is provided by external sources and is passed through the system by use of essentially nonsacrificial anodes such as carbon, noncorrodible alloys, or platinum buried in the ground or suspended in the electrolyte in the case of aqueous systems.

The requirements with respect to current distribution and anode placement vary with the resistivity of soils or the electrolyte involved.

Anodic Protection This electrochemical method relies on an external potential control system (potentiostat) to maintain the metal or alloy in a noncorroding (passive) condition. Practical applications include acid coolers in sulfuric acid plants and storage tanks for sulfuric acid.

Coatings and Linings The use of nonmetallic coatings and lining materials in combination with steel or other materials has and will continue to be an important type of construction for combating corrosion.

Organic coatings of many kinds are used as linings in equipment such as tanks, piping, pumping lines, and shipping containers, and they are often an economical means of controlling corrosion, particularly when freedom from metal contamination is the principal objective. One principle that is now generally accepted is that thin nonreinforced paintlike coatings of less than 0.75-mm (0.03-in) thickness should not be used in services for which full protection is required in order to prevent rapid attack of the substrate metal. This is true because most thin coatings contain defects or holidays and can be easily damaged in service, thus leading to early failures due to corrosion of the substrate metal even though the coating material is resistant. Electrical testing for continuity of coating-type linings is always desirable for immersion-service applications in order to detect holiday-type defects in the coating.

The most dependable barrier linings for corrosive services are those which are bonded directly to the substrate and are built up in multiple-layer or laminated effects to thicknesses greater than 2.5 mm (0.10 in). These include flake-glass-reinforced resin systems and elastomeric and plasticized plastic systems. Good surface preparation and thorough inspections of the completed lining, including electrical testing, should be considered as minimum requirements for any lining applications.

Linings of this type are slightly permeable to many liquids. Such permeation, while not damaging to the lining, may cause failure by causing disbonding of the lining owing to pressure buildup between the lining and the steel.

Ceramic or carbon-brick linings are frequently used as facing linings over plastic or membrane linings when surface temperatures exceed those which can be handled by the unprotected materials or when the membrane must be protected from mechanical damage. This type of construction permits processing of materials that are too corrosive to be handled in low-cost metal constructions.

Glass-Lined Steel By proprietary methods, special glasses can be bonded to steel, providing an impervious liner 1.5 to 2.5 mm (0.060 to 0.100 in) thick. Equipment and piping lined in this manner are routinely used in severely corrosive acid services. The glass lining can be mechanically damaged, and careful attention to details of design, inspection, installation, and maintenance is required to achieve good results with this system.

The cladding of steel with an alloy is another approach to this problem. There are a number of cladding methods in general use. In one, a sandwich is made of the corrosion-resistant metal and carbon steel by hot rolling to produce a **pressure weld** between the plates.

Another process involves **explosive bonding.** The corrosion-resistant metal is bonded to a steel backing metal by the force generated by properly positioned explosive charges. Relatively thick sections of metal can be bonded by this technique into plates.

In a third process, a **loose liner** is fastened to a carbon steel shell by welds spaced so as to prevent collapse of the liner. A fourth method is **weld overlay,** which involves depositing multiple layers of alloy weld metal to cover the steel surface.

All these methods require careful design and control of fabrication methods to assure success.

Metallic Linings for Mild Environments **Zinc coatings** applied by various means have good corrosion resistance to many atmospheres. Such coatings have been extensively used on steel. Zinc has the advantage of being anodic to steel and therefore will protect exposed areas of steel by electrochemical action.

Steel coated with tin (**tinplate**) is used to make food containers. Tin is more noble than steel; therefore, well-aerated solutions will galvanically accelerate attack of the steel at exposed areas. The comparative absence of air within food containers aids in preserving the tin as well as the food. Also the reversible potential which the tin-iron couple undergoes in organic acids serves to protect exposed steel in food containers.

Cadmium, being anodic to steel, behaves quite similarly to zinc in providing corrosion protection when applied as a coating on steel. Tests of zinc and cadmium coatings should be conducted when it becomes necessary to determine the most economical selection for a particular environment.

Lead has a good general resistance to various atmospheres. As a coating, it has had its greatest application in the production of terneplate, which is used as a roofing, cornicing, and spouting material.

Aluminum coatings on steel will perform in a manner similar to zinc coatings. Aluminum has good resistance to many atmospheres; in addition, being anodic to steel, it will galvanically protect exposed areas. Aluminum-coated steel products are quite serviceable under high-temperature conditions, for which good oxidation resistance is required.

CORROSION-TESTING METHODS*

The primary purpose of materials selection is to provide the optimum equipment for a process application in terms of materials of construction, design, and corrosion-control measures. *Optimum* here means that which comprises the best combination of cost, life, safety, and reliability.

The selection of materials to be used in design dictates a basic understanding of the behavior of materials and the principles that govern such behavior. If proper design of suitable materials of construction is incorporated, the equipment should deteriorate at a uniform and anticipated gradual rate, which will allow scheduled maintenance or replacement at regular intervals. If localized forms of corrosion are characteristic of the combination of materials and environment, the materials engineer should still be able to predict the probable life of equipment, or devise an appropriate inspection schedule to preclude unexpected failures. The concepts of predictive, or at least preventive, maintenance are minimum requirements to proper materials selection. This approach to maintenance is certainly intended to minimize the possibility of unscheduled production shutdowns because of corrosion failures, with their attendant possible financial losses, hazard to personnel and equipment, and resultant environmental pollution.

Chemical processes may involve a complex variety of both inorganic and organic chemicals. Hard and fast rules for selecting the appropriate materials of construction can be given when the composition is known, constant, and free of unsuspected contaminates; when the relevant parameters of temperature, pressure, velocity, and concentra-

* Includes information excerpted from papers by Oliver W. Siebert, John G. Stoecker II, and Ann Chidester Van Orden, courtesy of NACE International; and Oliver W. Siebert, courtesy ASTM.

tion are defined; and when the mechanical and environmental degradation of the material is uniform, that is, free of localized attack. For example, it is relatively simple to select the materials of construction for a regimen of equipment for the storage and handling of cold, concentrated sulfuric acid. On the other hand, the choice of suitable materials for producing phosphoric acid by the digestion of phosphate rock with sulfuric acid is much more difficult because of the diversity in kind and concentration of contaminants, the temperatures of the reactions, and the strength of sulfuric and phosphoric acid used or formed. Probably the best way to approach the study of materials selection is to categorize the types of major chemicals that might be encountered, describe their inherent characteristics, and generalize about the corrosion characteristics of the prominent materials of construction in such environments.

The background information that materials selection is based on is derived from a number of sources. In many cases, information as to the corrosion resistance of a material in a specific environment is not available and must be derived experimentally. It is to this need that the primary remarks of this subsection are addressed.

Unfortunately, there is no standard or preferred way to evaluate an alloy in an environment. While the chemistry of the operating plant environment can sometimes be duplicated in the laboratory, factors of velocity, hot and cold wall effects, crevice, chemical reaction of the fluid during the test, stress levels of the equipment, contamination with products of corrosion, trace impurities, dissolved gases, and so forth also have a controlling effect on the quality of the answer. Then, too, the progress of the corrosion reaction itself varies with time. Notwithstanding, immersion testing remains the most widely used method for selecting materials of construction.

There is no standard or preferred way to carry out a corrosion test; the method must be chosen to suit the purpose of the test. The principal types of tests are, in decreasing order of reliability:

1. Actual operating experience with full-scale plant equipment exposed to the corroding medium.
2. Small-scale plant-equipment experience, under either commercial or pilot-plant conditions.
3. Sample tests in the field. These include coupons, stressed samples, electrical-resistance probes exposed to the plant corroding medium, or samples exposed to the atmosphere, to soils, or to fresh, brackish, or saline waters.
4. Laboratory tests on samples exposed to "actual" plant liquids or simulated environments.

Plant or field corrosion tests are useful for:

1. Selection of the most suitable material to withstand a particular environment and to estimate its probable durability in that environment
2. Study of the effectiveness of means of preventing corrosion

CORROSION TESTING: LABORATORY TESTS

Metals and alloys do not respond alike to all the influences of the many factors that are involved in corrosion. Consequently, it is impractical to establish any universal standard laboratory procedures for corrosion testing except for inspection tests. However, some details of laboratory testing need careful attention in order to achieve useful results.

In the selection of materials for the construction of a chemical plant, resistance to the corroding medium is often the determining factor; otherwise, the choice will fall automatically on the cheapest material mechanically suitable. Laboratory corrosion tests are frequently the quickest and most satisfactory means of arriving at a preliminary selection of the most suitable materials to use. Unfortunately, however, it is not yet within the state of the art of laboratory tests to predict with accuracy the behavior of the selected material under plant-operating conditions. The outstanding difficulty lies not so much in carrying out the test as in interpreting the results and translating them into terms of plant performance. A laboratory test of the conventional type gives mainly one factor—the chemical resistance of the proposed material to the corrosive agent. There are numerous other factors entering into the behavior of the material in the plant, such as dissolved gases, velocity, turbulence, abrasion, crevice conditions, hot-wall effects, cold-wall effects, stress levels of metals, trace impurities in corrodent that act as corrosion inhibitors or accelerators, and variations in composition of corrodent.

Immersion Test One method of determining the chemical-resistance factor, the so-called **total-immersion test,** represents an unaccelerated method that has been found to give reasonably concordant results in approximate agreement with results obtained on the large scale when the other variables are taken into account. Various other tests have been proposed and are in use, such as salt-spray, accelerated electrolytic, alternate-immersion, and aerated-total-immersion; but in view of the numerous complications entering into the translation of laboratory results into plant results the simplest test is considered the most desirable for routine preliminary work, reserving special test methods for special cases. The total-immersion test serves quite well to eliminate materials that obviously cannot be used; further selection among those materials which apparently can be used can be made on the basis of a knowledge of the properties of the materials concerned and the working conditions or by constructing larger-scale equipment of the proposed materials in which the operating conditions can be simulated.

The National Association of Corrosion Engineers (NACE) TMO169-95 "Standard Laboratory Corrosion Testing of Metals for the Process Industries," and ASTM G31 "Recommended Practice for Laboratory Immersion Corrosion Testing of Metals" are the general guides for immersion testing. Small pieces of the candidate metal are exposed to the medium, and the loss of mass of the metal is measured for a given period of time. Immersion testing remains the best method to eliminate from further consideration those materials that obviously cannot be used. This technique is frequently the quickest and most satisfactory method of making a preliminary selection of the best candidate materials.

Probably the most serious disadvantage of this method of corrosion study is the assumed average-time weight loss. The corrosion rate could be high initially and then decrease with time (it could fall to zero). In other cases the rate of corrosion might increase very gradually with time or it could cycle or be some combination of these things.

The description that follows is based on these standards.

Test Piece The size and the shape of specimens will vary with the purpose of the test, nature of the material, and apparatus used. A large surface-to-mass ratio and a small ratio of edge area to total area are desirable. These ratios can be achieved through the use of rectangular or circular specimens of minimum thickness. Circular specimens should be cut preferably from sheet and not bar stock to minimize the exposed end grain.

A circular specimen of about 38-mm (1.5-in) diameter is a convenient shape for laboratory corrosion tests. With a thickness of approximately 3 mm (⅛ in) and an 8- or 11-mm- (5/16- or 7/16-in-) diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the equation:

$$A = \frac{\pi}{2}(D^2 - d^2) + t\pi D + t\pi d$$

where t = thickness, D = diameter of the specimen, and d = diameter of the mounting hole. If the hole is completely covered by the mounting support, the final term ($t\pi d$) in the equation is omitted.

Strip coupons [50 by 25 by 1.6 or 3.2 mm (2 by 1 by 1/16 or ⅛ in)] may be preferred as corrosion specimens, particularly if interface or liquid-line effects are to be studied by the laboratory test.

All specimens should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to plus or minus 1 percent is usually adequate.

More uniform results may be expected if a substantial layer of metal is removed from the specimens to eliminate variations in condition of the original metallic surface. This can be done by chemical treatment (pickling), electrolytic removal, or grinding with a coarse abrasive paper or cloth, such as No. 50, using care not to work-harden the surface. At least 2.5×10^{-3} mm (0.0001 in) or 1.5 to 2.3 mg/cm^2 (10 to 15 mg/in^2) should be removed. If clad alloy specimens are to be used, special attention must be given to ensure that excessive metal is not removed. After final preparation of the specimen surface, the speci-

mens should be stored in a desiccator until exposure if they are not used immediately.

Specimens should be finally degreased by scrubbing with bleach-free scouring powder, followed by thorough rinsing in water and in a suitable solvent (such as acetone, methanol, or a mixture of 50 percent methanol and 50 percent ether), and air-dried. For relatively soft metals such as aluminum, magnesium, and copper, scrubbing with abrasive powder is not always needed and can mar the surface of the specimen. The use of towels for drying may introduce an error through contamination of the specimens with grease or lint. The dried specimen should be weighed on an analytic balance.

Apparatus A versatile and convenient apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5,000 mL), a reflux condenser with atmospheric seal, a sparger for controlling atmosphere or aeration, a thermowell and temperature-regulating device, a heating device (mantle, hot plate, or bath), and a specimen-support system. If agitation is required the apparatus can be modified to accept a suitable stirring mechanism such as a magnetic stirrer. A typical resin-flask setup for this type of test is shown in Fig. 28-3. Open-beaker tests should not be used because of evaporation and contamination.

In more complex tests, provisions might be needed for continuous flow or replenishment of the corrosive liquid while simultaneously maintaining a controlled atmosphere.

Apparatus for testing materials for heat-transfer applications is shown in Fig. 28-4. Here the sample is at a higher temperature than the bulk solution.

If the test is to be a guide for the selection of a material for a particular purpose, the limits of controlling factors in service must be determined. These factors include oxygen concentration, temperature, rate of flow, pH value, and other important characteristics.

The **composition of the test solution** should be controlled to the fullest extent possible and be described as thoroughly and as accurately as possible when the results are reported. Minor constituents should not be overlooked because they often affect corrosion rates. Chemical content should be reported as percentage by weight of the solution. Molarity and normality are also helpful in defining the concentration of chemicals in the test solution. The composition of the test solution should be checked by analysis at the end of the test to determine the extent of change in composition, such as might result from evaporation.

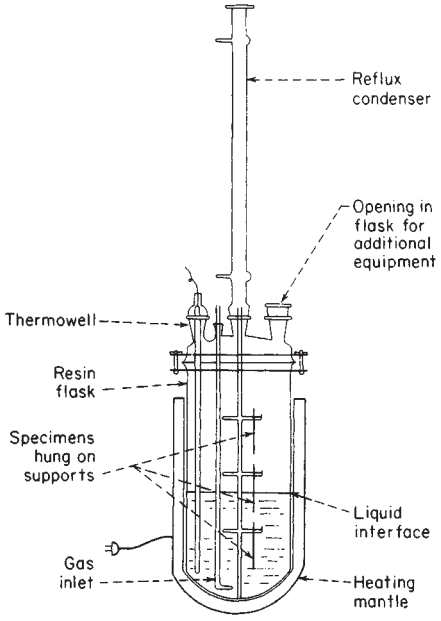


FIG. 28-3 Laboratory-equipment arrangement for corrosion testing. (*Based on NACE Standard TMO169-95.*)

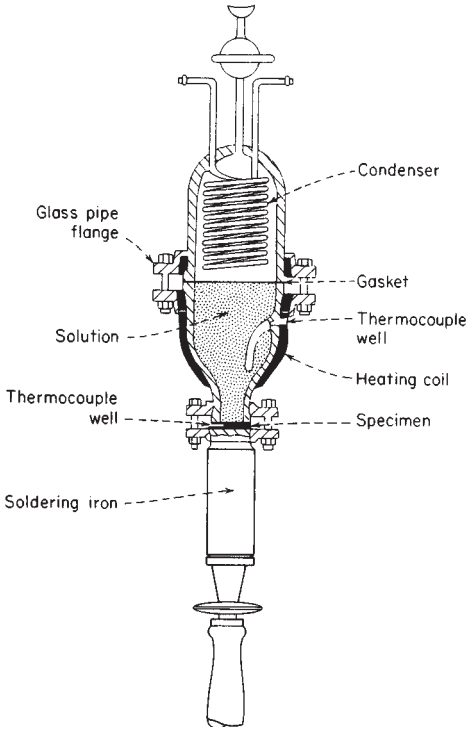


FIG. 28-4 Laboratory setup for the corrosion testing of heat-transfer materials.

Temperature of Solution Temperature of the corroding solution should be controlled within ±1°C (±1.8°F) and must be stated in the report of test results.

For tests at ambient temperatures, the tests should be conducted at the highest temperature anticipated for stagnant storage in summer months. This temperature may be as high as 40 to 45°C (104 to 113°F) in some localities. The variation in temperature should be reported also (e.g., 40°C ± 2°C).

Aeration of Solution Unless specified, the solution should not be aerated. Most tests related to process equipment should be run with the natural atmosphere inherent in the process, such as the vapors of the boiling liquid. If aeration is used, the specimens should not be located in the direct air stream from the sparger. Extraneous effects can be encountered if the air stream impinges on the specimens.

Solution Velocity The effect of velocity is not usually determined in laboratory tests, although specific tests have been designed for this purpose. However, for the sake of reproducibility some velocity control is desirable.

Tests at the boiling point should be conducted with minimum possible heat input, and boiling chips should be used to avoid excessive turbulence and bubble impingement. In tests conducted below the boiling point, thermal convection generally is the only source of liquid velocity. In test solutions of high viscosities, supplemental controlled stirring with a magnetic stirrer is recommended.

Volume of Solution Volume of the test solution should be large enough to avoid any appreciable change in its corrosiveness through either exhaustion of corrosive constituents or accumulation of corrosion products that might affect further corrosion.

A suitable volume-to-area ratio is 20 mL (125 mL) of solution/cm^2 (in^2) of specimen surface. This corresponds to the recommendation of ASTM Standard A262 for the Huey test. The preferred volume-to-

area ratio is 40 mL/cm^2 (250 mL/in^2) of specimen surface, as stipulated in ASTM Standard G31, Laboratory Immersion Testing of Materials.

Method of Supporting Specimens The supporting device and container should not be affected by or cause contamination of the test solution. The method of supporting specimens will vary with the apparatus used for conducting the test but should be designed to insulate the specimens from each other physically and electrically and to insulate the specimens from any metallic container or supporting device used with the apparatus.

Shape and form of the specimen support should assure free contact of the specimen with the corroding solution, the liquid line, or the vapor phase, as shown in Fig. 28-3. If clad alloys are exposed, special procedures are required to ensure that only the cladding is exposed (unless the purpose is to test the ability of the cladding to protect cut edges in the test solution). Some common supports are glass or ceramic rods, glass saddles, glass hooks, fluorocarbon plastic strings, and various insulated or coated metallic supports.

Duration of Test Although the duration of any test will be determined by the nature and purpose of the test, an excellent procedure for evaluating the effect of time on corrosion of the metal and also on the corrosiveness of the environment in laboratory tests has been presented by Wachter and Treseder [*Chem. Eng. Prog.,* 315–326 (June 1947)]. This technique is called the **planned-interval test.** Other procedures that require the removal of solid corrosion products between exposure periods will not measure accurately the normal changes of corrosion with time.

Materials that experience severe corrosion generally do not need lengthy tests to obtain accurate corrosion rates. Although this assumption is valid in many cases, there are exceptions. For example, lead exposed to sulfuric acid corrodes at an extremely high rate at first while building a protective film; then the rate decreases considerably, so that further corrosion is negligible. The phenomenon of forming a protective film is observed with many corrosion-resistant materials, and therefore short tests on such materials would indicate high corrosion rates and would be completely misleading.

Short-time tests also can give misleading results on alloys that form passive films, such as stainless steels. With borderline conditions, a prolonged test may be needed to permit breakdown of the passive film and subsequently more rapid attack. Consequently, tests run for long periods are considerably more realistic than those conducted for short durations. This statement must be qualified by stating that corrosion should not proceed to the point at which the original specimen size or the exposed area is drastically reduced or the metal is perforated.

If anticipated corrosion rates are moderate or low, the following equation gives a suggested test duration:

$$\text{Duration of test, h} = \frac{78{,}740}{\text{corrosion rate, mm/y}}$$

$$= \frac{2000}{\text{corrosion rate, mils/y}}$$

Cleaning Specimens after Test Before specimens are cleaned, their appearance should be observed and recorded. Locations of deposits, variations in types of deposits, and variations in corrosion products are extremely important in evaluating localized corrosion such as pitting and concentration-cell attack.

Cleaning specimens after the test is a vital step in the corrosion-test procedure and, if not done properly, can give rise to misleading test results. Generally, the cleaning procedure should remove all corrosion products from specimens with a minimum removal of sound metal. Set rules cannot be applied to cleaning because procedures will vary with the type of metal being cleaned and the degree of adherence of corrosion products.

Mechanical cleaning includes scrubbing, scraping, brushing, mechanical shocking, and ultrasonic procedures. Scrubbing with a bristle brush and a mild abrasive is the most widely used of these methods; the others are used principally as supplements to remove heavily encrusted corrosion products before scrubbing. Care should be used to avoid the removal of sound metal.

Chemical cleaning implies the removal of material from the surface of the specimen by dissolution in an appropriate chemical agent. Solvents such as acetone, carbon tetrachloride, and alcohol are used to remove oil, grease, or resin and are usually applied prior to other methods of cleaning. Various chemicals are chosen for application to specific materials; some of these treatments in general use are outlined in the NACE standard.

Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that has been found to be useful for many metals and alloys is as follows:

Solution: 5 percent (by weight) H_2SO_4
Anode: carbon or lead
Cathode: test specimen
Cathode current density: 20 A/dm^2 (129 A/in^2)
Inhibitor: 2 cm^3 organic inhibitor per liter
Temperature: 74°C (165°F)
Exposure period: 3 min

Precautions must be taken to ensure good electrical contact with the specimen, to avoid contamination of the solution with easily reducible metal ions, and to ensure that inhibitor decomposition has not occurred. Instead of using 2 mL of any proprietary inhibitor, 0.5 g/L of inhibitors such as diorthotolyl thiourea or quinoline ethiodide can be used.

Whatever treatment is used to clean specimens after a corrosion test, its effect in removing metal should be determined, and the weight loss should be corrected accordingly. A "blank" specimen should be weighed before and after exposure to the cleaning procedure to establish this weight loss.

Evaluation of Results After the specimens have been reweighed, they should be examined carefully. Localized attack such as pits, crevice corrosion, stress-accelerated corrosion, cracking, or intergranular corrosion should be measured for depth and area affected.

Depth of localized corrosion should be reported for the actual test period and not interpolated or extrapolated to an annual rate. The rate of initiation or propagation of pits is seldom uniform. The size, shape, and distribution of pits should be noted. A distinction should be made between those occurring underneath the supporting devices (concentration cells) and those on the surfaces that were freely exposed to the test solution. An excellent discussion of pitting corrosion has been published [*Corrosion,* 25t (January 1950)].

The specimen may be subjected to simple bending tests to determine whether any **embrittlement** has occurred.

If it is assumed that localized or internal corrosion is not present or is recorded separately in the report, the **corrosion rate** or penetration can be calculated alternatively as

$$\frac{\text{Weight loss} \times 534}{(\text{Area})(\text{time})(\text{metal density})} = \text{mils/y (mpy)}$$

$$\frac{\text{Weight loss} \times 13.56}{(\text{Area})(\text{time})(\text{metal density})} = \text{mm/y (mmpy)}$$

where weight loss is in mg, area is in in^2 of metal surface exposed, time is in hours exposed, and density is in g/cm^3. Densities for alloys can be obtained from the producers or from various metal handbooks.

The following **checklist** is a recommended guide for reporting all **important information and data:**

Corrosive media and concentration (changes during test)
Volume of test solution
Temperature (maximum, minimum, and average)
Aeration (describe conditions or technique)
Agitation (describe conditions or technique)
Type of apparatus used for test
Duration of each test (start, finish)
Chemical composition or trade name of metals tested
Form and metallurgical conditions of specimens
Exact size, shape, and area of specimens
Treatment used to prepare specimens for test
Number of specimens of each material tested and whether specimens were tested separately or which specimens were tested in the same container

Method used to clean specimens after exposure and the extent of any error expected by this treatment

Actual weight losses for each specimen

Evaluation of attack if other than general, such as crevice corrosion under support rod, pit depth and distribution, and results of microscopic examination or bend tests

Corrosion rates for each specimen expressed as millimeters (mils) per year

Effect of Variables on Corrosion Tests It is advisable to apply a factor of safety to the results obtained, the factor varying with the degree of confidence in the applicability of the results. Ordinarily, a factor of from 3 to 10 might be considered normal.

Among the more important points that should be considered in attempting to base plant design on laboratory corrosion-rate data are the following.

Galvanic corrosion is a frequent source of trouble on a large scale. Not only is the use of different metals in the same piece of equipment dangerous, but the effect of cold working may be sufficient to establish potential differences of objectionable magnitude between different parts of the same piece of metal. The mass of metal in chemical apparatus is ordinarily so great and the electrical resistance consequently so low that a very small voltage can cause a very high current. Welding also may leave a weld of a different physical or chemical composition from that of the body of the sheet and cause localized corrosion.

Local variations in temperature and crevices that permit the accumulation of corrosion products are capable of allowing the formation of **concentration cells,** with the result of accelerated local corrosion.

In the laboratory, the **temperature** of the test specimen is that of the liquid in which it is immersed, and the measured temperature is actually that at which the reaction is taking place. In the plant (heat being supplied through the metal to the liquid in many cases), the temperature of the film of (corrosive) liquid on the inside of the vessel may be a number of degrees higher than that registered by the thermometer. As the relation between temperature and corrosion is a logarithmic one, the rate of increase is very rapid. Like other chemical reactions, the speed ordinarily increases twofold to threefold for each 10°C temperature rise, the actual relation being that of the equation $\log K = A + (B/T)$, where K represents the rate of corrosion and T the absolute temperature. This relationship, although expressed mathematically, must be understood to be a qualitative rather than strictly a quantitative one.

Cold walls, as in coolers or condensers, usually have somewhat decreased corrosion rates for the reason just described. However, in some cases, the decrease in temperature may allow the formation of a more corrosive second phase, thereby increasing corrosion.

The effect of **impurities** in either structural material or corrosive material is so marked (while at the same time it may be either accelerating or decelerating) that for reliable results the actual materials which it is proposed to use should be tested and not types of these materials. In other words, it is much more desirable to test the actual plant solution and the actual metal or nonmetal than to rely upon a duplication of either. Since as little as 0.01 percent of certain organic compounds will reduce the rate of solution of steel in sulfuric acid 99.5 percent and 0.05 percent bismuth in lead will increase the rate of corrosion over 1000 percent under certain conditions, it can be seen how difficult it would be to attempt to duplicate here all the significant constituents.

Electrical Resistance The measurement of corrosion by electrical resistance is possible by considering the change in resistance of a thin metallic wire or strip sensing element (probe) as its cross section decreases from a loss of metal. Since small changes in resistance are encountered as corrosion progresses, changes in temperature can cause enough change in the wire resistance to complicate the results. Commercial equipment, such as the Corrosometer®, have a protected reference section of the specimen in the modified electrical Wheatstone bridge (Kelvin) circuit to compensate for these temperature changes. Since changes in the resistance ratio of the probe are not linear with loss of section thickness, compensation for this variable must be included in the circuit. In operation, the specimen probe is exposed to the environment and instrument readings are periodically recorded. The corrosion rate is the loss of metal averaged between any two readings.

The corrosion rate can be studied by this method over very short periods of time, but not instantaneously. The environment does not have to be an electrolyte. Studies can be made in corrosive gas exposures. The main disadvantage of the technique is that local corrosion (pitting, crevice corrosion, galvanic, stress corrosion cracking, fatigue, and so forth) will probably not be progressively identified. If the corrosion product has an electrical conductivity approaching that of the lost metal, little or no corrosion will be indicated. The same problem will result from the formation of conducting deposits on the specimen.

The electrical-resistance measurement has nothing to do with the electrochemistry of the corrosion reaction. It merely measures a bulk property that is dependent upon the specimen's cross-section area. Commercial instruments are available (Fig. 28-5).

Advantages of the electrical-resistance technique are:

1. A corrosion measurement can be made without having to see or remove the test sample.
2. Corrosion measurements can be made quickly—in a few hours or days, or continuously. This enables sudden increases in corrosion rate to be detected. In some cases, it will be possible then to modify the process to decrease the corrosion.
3. The method can be used to monitor a process to indicate whether the corrosion rate is dependent on some critical process variable.
4. Corrodent need not be an electrolyte (in fact, need not be a liquid).
5. The method can detect low corrosion rates that would take a long time to detect with weight-loss methods.

Limitations of the technique are:

1. It is usually limited to the measurement of uniform corrosion only and is not generally satisfactory for localized corrosion.
2. The probe design includes provisions to compensate for temperature variations. This feature is not totally successful. The most reliable results are obtained in constant-temperature systems.

EMF versus pH (Pourbaix) Diagrams Potential (EMF) versus pH equilibrium (Pourbaix) diagrams derived from physical property data about the metal and its environment provide a basis for the expression of a great amount of thermodynamic data about the corrosion reaction. These relatively simple diagrams graphically represent the thermodynamics of corrosion in terms of electromotive force, that is, an indication of oxidizing power and pH, or acidity. As an aid in corrosion prediction, their usefulness lies in providing direction for establishing a corrosion study program.

Figure 28-6 is a typical Pourbaix diagram. Generally, the diagrams show regions of immunity (the metal), passivity (the surface film), and corrosion (metallic ions). While of considerable qualitative usefulness, these diagrams have important limitations. Since they are calculated from thermodynamic properties, they represent equilibrium conditions and do not provide kinetic information. Thus, while they show conditions where corrosion will not occur, they do not necessarily indicate under what conditions corrosion will occur. To determine the quantitative value of corrosion, kinetic rate measurement would still be required. Pourbaix diagrams were developed for the study of pure metals. Since few engineering structures are made of pure metals, it is

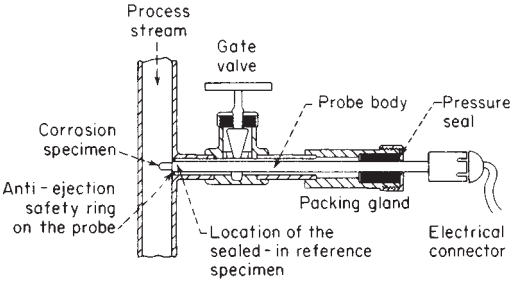


FIG. 28-5 Typical retractable corrosion probe.

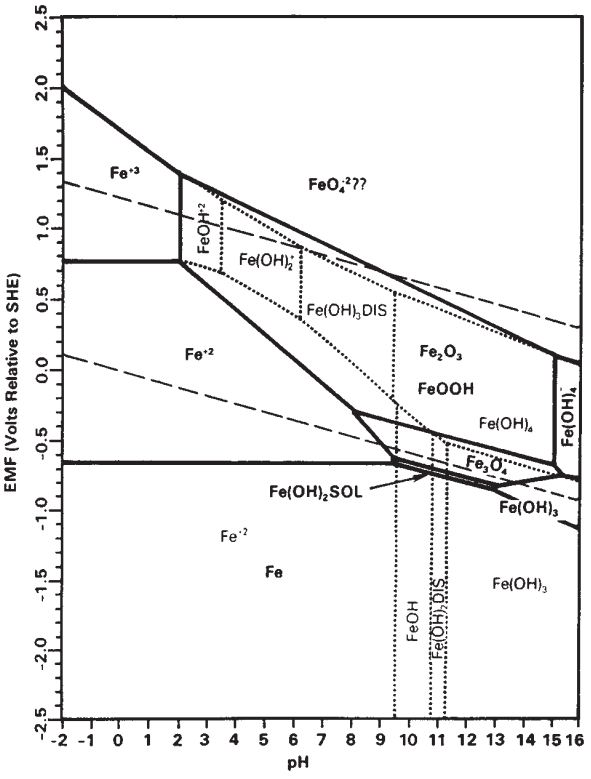


FIG. 28-6 EMF-pH diagram for an iron-water system at 25°C. All ions are at an activity of 10^{-6}.

important to extend this technique to include information on the passive behavior of alloys of engineering interest. Values of the open circuit corrosion potential (OCP) or a controlled potential occur, if a steady site potential can be used in conjunction with the solution pH and these diagrams to show what component is stable in the system defined by a given pH and potential. Theoretical diagrams so developed estimate the corrosion product in various regions. The use of computers to construct diagrams for alloy systems provides an opportunity to mathematically overcome many of the limitations inherent in the pure metal system.

A potentiokinetic electrochemical hysteresis method of diagram construction has led to consideration of three-dimensional Pourbaix diagrams for alloy systems useful in alloy development, evaluation of the influence of crevices, prediction of the tendency for dealloying, and the inclusion of kinetic data on the diagram is useful in predicting corrosion rather than just the absence of damage. These diagrams are kinetic, not thermodynamic, expressions. The two should not be confused as being the same reaction, as they are not.

Tafel Extrapolation Corrosion is an electrochemical reaction of a metal and its environment. When corrosion occurs, the current that flows between individual small anodes and cathodes on the metal surface causes the electrode potential for the system to change. While this current cannot be measured, it can be evaluated indirectly on a metal specimen with an inert electrode and an external electrical circuit. Polarization is described as the extent of the change in potential of an electrode from its equilibrium potential caused by a net current flow to or from the electrode, galvanic or impressed (Fig. 28-7).

Electrochemical techniques have been used for years to study fundamental phenomenological corrosion reactions of metals in corrosive environments. Unfortunately, the learning curve in the reduction of these electrochemical theories to practice has been painfully slow. However, a recent survey has shown that many organizations in the

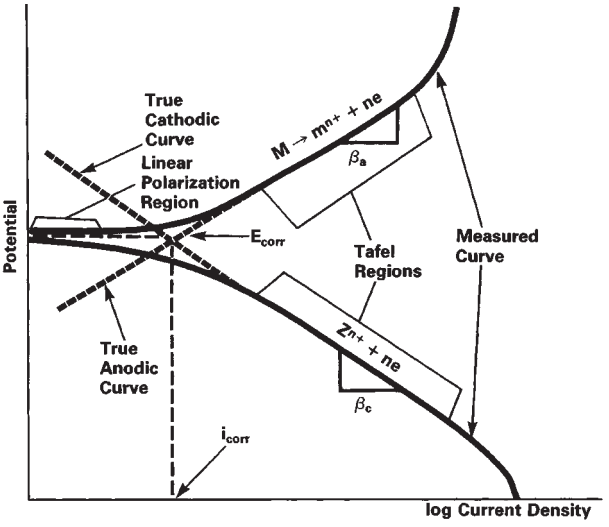


FIG. 28-7 Tafel extrapolation and linear polarization curves.

chemical process industries are now adding electrochemical methods to their materials selection techniques. Laboratory electrochemical tests of metal/environment systems are being used to show the degree of compatibility and describe the limitations of those relationships. The general methods being used include electrical resistance, Tafel extrapolation, linear polarization, and both slow and rapid-scan potentiodynamic polarization. Depending upon the study technique used, it has also been possible to indicate the tendency of a given system to suffer local pitting or crevice attack or both. These same tools have been the basis of design protection of less-noble structural metals.

To study the anode reaction of a specimen in an environment, sufficient current is applied to change the freely corroding potential of the metal in a more electropositive direction with respect to the inert electrode (acting as a cathode). The opposite of this so-called anodic polarization is cathodic polarization. Polarization can be studied equally well by varying the potential and measuring the resultant changes in the current. Both of the theoretical (true) polarization curves are straight lines when plotted on a semilog axis. The corrosion current can be measured from the intersection of the corrosion potential and either the anodic or cathodic curve. The corrosion rate of the system is a function of that corrosion current. Experimentally derived curves are not fully linear because of the interference from the reactions between the anodes and cathodes in the region close to the corrosion potential. IR losses often obscure the Tafel behavior. Away from the corrosion potential, the measured curves match the theoretical (true) curves. The matching region of the measured curves is called the **Tafel region,** and their (Tafel) slopes are constant. Corrosion rates can be calculated from the intersection of the corrosion potential and the extrapolation of the Tafel region. The main advantage of the technique is that it is quick; curves can be generated in about an hour.

The technique is of limited value where more than one cathodic reduction reaction occurs. In most cases it is difficult to identify a sufficient linear segment of the Tafel region to extrapolate accurately. Since currents in the Tafel region are one to two orders of magnitude larger on the log scale than the corrosion current, relatively large currents are required to change the potentials from what they are at the corrosion potential. The environment must be a conductive solution. The Tafel technique does not indicate local attack, only an average, uniform corrosion rate.

The primary use of this laboratory technique today is as a quick check to determine the order of magnitude of a corrosion reaction. Sometimes the calculated rate from an immersion test does not "look" correct when compared to the visual appearance of the metal coupon.

While the specific corrosion rate number determined by Tafel extrapolation is seldom accurate, the method remains a good confirmation tool.

Linear Polarization Some of the limitations of the Tafel extrapolation method can be overcome by using the linear-polarization technique to determine the corrosion rate. A relationship exists between the slope of the polarization curves *E/I* (with units of resistance, linear polarization is sometimes termed *polarization resistance*) and instantaneous corrosion rates of a freely corroding alloy. The polarization resistance is determined by measuring the amount of applied current needed to change the corrosion potential of the freely corroding specimen by about 10-mV deviations. The slope of the curves thus generated is directly related to the corrosion rate by Faraday's law. Several instruments are available that are used in linear polarization work. The main advantage is that each reading on the instrument can be translated directly into a corrosion rate.

As with all electrochemical studies, the environment must be electrically conductive. The corrosion rate is directly dependent on the Tafel slope. The Tafel slope varies quite widely with the particular corroding system and generally with the metal under test. As with the Tafel extrapolation technique, the Tafel slope generally used is an assumed, more or less average value. Again, as with the Tafel technique, the method is not sensitive to local corrosion.

The amount of externally applied current needed to change the corrosion potential of a freely corroding specimen by a few millivolts (usually 10 mV) is measured. This current is related to the corrosion current, and therefore the corrosion rate, of the sample. If the metal is corroding rapidly, a large external current is needed to change its potential, and vice versa.

The measuring system consists of four basic elements:

1. *Electrodes.* Test and reference electrodes and, in some cases, an auxiliary electrode.
2. *Probe.* It connects the electrodes in the corrodent on the inside of a vessel to the electrical leads.
3. *Electrical leads.* They run from the probe to the current source and instrument panel.
4. *Control system.* Current source (batteries), ammeter, voltmeter, instrument panel, and so on.

Commercial instruments have either two or three electrodes. Also, there are different types of three-electrode systems. The application and limitations of the instruments are largely dependent upon these electrode systems.

Potentiodynamic Polarization Not all metals and alloys react in a consistent manner in contact with corrosive fluids. One of the common intermediate reactions of a metal (surface) is with oxygen, and those reactions are variable and complex. Oxygen can sometimes function as an electron acceptor; that is, oxygen can act as an oxidizing agent, and remove the "protective" film of hydrogen from the cathodic area, **cathodic depolarization.** The activation energy of the oxygen/hydrogen reaction is very large. This reaction does not normally occur at room temperature at any measureable rate. In other cases, oxygen can form protective oxide films. The long-term stability of these oxides also varies; some are soluble in the environment, others form more stable and inert or passive films.

Because corrosion is an electrochemical process, it is possible to evaluate the overall reaction by the use of an external electrical circuit called a **potentiostat.** When corrosion occurs, a potential difference exists between the metal and its ions in solution. It is possible to electrically control this potential; changes in potential cause changes in current (corrosion). Oxidation is a reaction with a loss of electrons (anodic—the reacting electrode is the anode); reduction is a reaction with a gain of electrons (cathodic—the reacting electrode is the cathode). Rather than allowing the electrons being evolved from the corrosion reaction to combine with hydrogen, these electrons can be removed by internal circuitry, and sent through a potentiostat, causing a cathodic (or anodic) reaction to occur at a platinum counter electrode. This is always true for the external polarization method; it is not unique for a potentiostat.

It is now well established that the activity of pitting, crevice corrosion, and stress-corrosion cracking is strongly dependent upon the corrosion potential (i.e., the potential difference between the corroding metal and a suitable reference electrode). By using readily available electronic equipment, the quantity and direction of direct current required to control the corrosion potential in a given solution at a given selected value can be measured. A plot of such values over a range of potentials is called a polarization diagram. By using proper experimental techniques, it is possible to define approximate ranges of corrosion potential in which pitting, crevice corrosion, and stress-corrosion cracking will or will not occur. With properly designed probes, these techniques can be used in the field as well as in the laboratory.

The potentiostat has a three-electrode system: a reference electrode, generally a saturated calomel electrode (SCE); a platinum counter, or auxiliary, electrode through which current flows to complete the circuit; and a working electrode that is a sample of interest (Fig. 28-8). The potentiostat is an instrument that allows control of the potential, either holding constant at a given potential, stepping from potential to potential, or changing the potential anodically or cathodically at some linear rate.

In the study of the anode/cathode polarization behavior of a metal/environment system, the potentiostat provides a plot of the relationship of current changes resulting from changes in potential most often presented as a plot of log current density versus potential, or Evans diagram. A typical active/passive metal anodic polarization curve is seen in Fig. 28-9, generally showing the regions of active corrosion and passivity and a transpassive region.

Scan Rates Sweeping a range of potentials in the anodic (more electropositive) direction of a potentiodynamic polarization curve at a high scan rate of about 60 V/h (high from the perspective of the corrosion engineer, slow from the perspective of a physical chemist) is to indicate regions where intense anodic activity is likely. Second, for otherwise identical conditions, sweeping at a relatively slow rate of potential change of about 1 V/h will indicate regions wherein relative inactivity is likely. The rapid sweep of the potential range has the object of minimizing film formation, so that the currents observed relate to relatively film-free or thin-film conditions. The object of the slow sweep rate experiment is to allow time for filming to occur. A zero scan rate provides the opportunity for maximum stability of the metal surface, but at high electropositive potentials the environment could be affected or changed. A rapid scan rate compromises the steady-state nature of the metal surface but better maintains the stability of the environment. Whenever possible, corrosion tests should be conducted using as many of the techniques available, potentiodynamic polarization at various scan rates, crevice, stress, velocity, and so

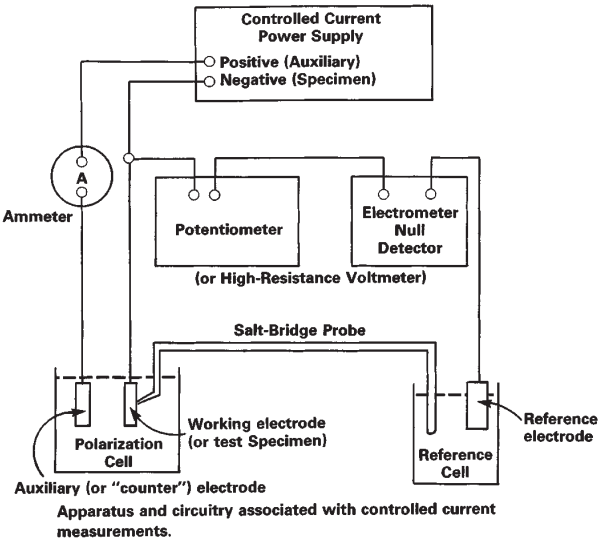


FIG. 28-8 The potentiostat apparatus and circuitry associated with controlled potential measurements of polarization curves.

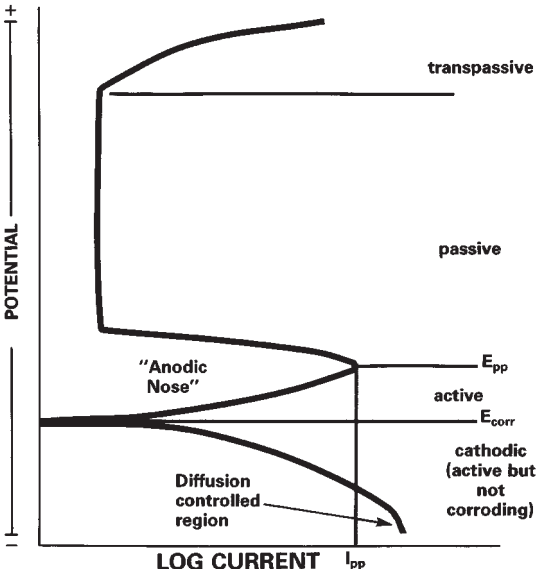


FIG. 28-9 Typical electrochemical polarization curve for an active/passive alloy (with cathodic trace) showing active, passive, and transpassive regions and other important features. (NOTE: E_{pp} = primary passive potential, E_{corr} = freely corroding potential).

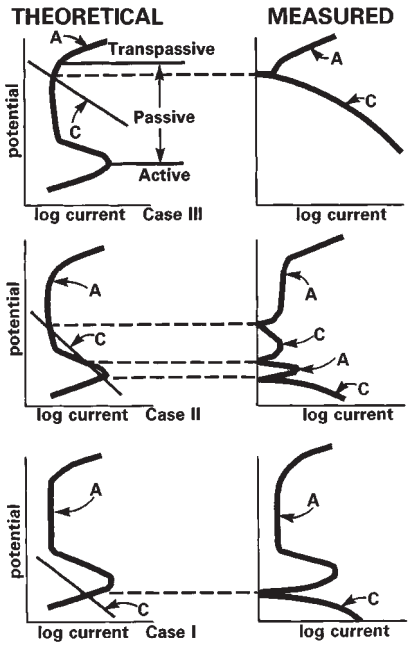


FIG. 28-10 Six possible types of behavior for an active/passive alloy in a corrosive environment.

forth. An evaluation of these several results, on a holistic basis, can greatly reduce or temper their individual limitations.

Slow-Scan Technique In ASTM G5 "Polarization Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements," all oxygen in the test solution is purged with hydrogen for a minimum of 0.5 h before introducing the specimen. The test material is then allowed to reach a steady state of equilibrium (open circuit corrosion potential, E_{corr}) with the test medium before the potential scan is conducted. Starting the evaluation of a basically passive alloy that is already in its "stable" condition precludes any detailed study of how the metal reaches that protected state (the normal intersection of the theoretical anodic and cathodic curves is recorded as a zero applied current on the ASTM potentiostatic potential versus applied current diagram). These intersections between the anodic and cathodic polarization curves are the condition where the total oxidation rate equals the total reduction rate (ASTM G3 "Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing").

Three general reaction types compare the activation-control reduction processes. In Fig. 28-10, in Case 1, the single reversible corrosion potential (anode/cathode intersection) is in the active region. A wide range of corrosion rates is possible. In Case 2, the cathodic curve intersects the anodic curve at three potentials, one active and two passive. If the middle active/passive intersection is not stable, the lower and upper intersections indicate the possibility of very high corrosion rates. In Case 3, corrosion is in the stable, passive region, and the alloys generally passivate spontaneously and exhibit low corrosion rates. Most investigators report that the ASTM method is effective for studying Case 1 systems. An alloy-medium system exhibiting Case 2 and 3 conditions generally cannot be evaluated by this conventional ASTM method.

The potentiodynamic polarization electrochemical technique can be used to study and interpret corrosion phenomena. It may also furnish useful information on film breakdown or repair.

Rapid-Scan Corrosion Behavior Diagram (CBD) Basically, all the same equipment used in the conductance of an ASTM G5 slow-scan polarization study is used for rapid-scan CBDs (that is, a standard test cell, potentiostat, voltmeters, log converters, X-Y recorders, and electronic potential scanning devices). The differences are in technique: the slow scan is run at a potential sweep rate of about 0.6 V/h; the rapid-scan CBDs at about 50 V/h.

In the conductance of rapid-scan CBDs, the test specimen is mechanically and chemically cleaned immediately before immersion in the test cell. Without any further delay, a cathodic polarization scan is made at a sweep rate of about 50 V/h (compared to the 0.6 V/h for the ASTM method). This rapid cathodic charging (hydrogen evolution) further cleans the specimen of oxygen so that the subsequent anodic polarization enables a full study of how the corrosion reaction progresses as the potential is changed potentiodynamically in the more noble (positive) direction without the interference of any preexisting passive or corrosion product film or scale. The test is run open to the atmosphere without any purge gas, and the rapid scan rate permits completion of the anodic curve before oxygen is replenished. This cathodic cleaning further activates the specimen and allows it to follow the pattern of its corrosion reaction(s) before it has an opportunity to spontaneously passivate or return to equilibrium with its environment.

Different from the slow-scan technique, which is generally limited to Case 1 alloy/medium systems, the rapid-scan technique allows full anodic polarization study of alloys showing all Case 1, 2, and 3 behavior. In Case 1, the single reversible corrosion potential (the anode/cathode intersection) is in the active region. A wide range of corrosion rates is possible. In Case 2, the cathodic curve intersects the anodic curve at three potentials, one in the active region and two in the passive. Since the middle active/passive intersection is not stable, the intersections indicate the possibility of very high corrosion rates depending on the environment or even slight changes to the exposure/environment system. In Case 3, the curves intersect in the most stable, passive region; the alloys generally passivate spontaneously and exhibit low corrosion rates. Case 2 exhibits the most corrosion, is difficult to study, and presents the most risk for materials of construction selection. Anything that can change the oxygen solubility of the oxidizing agent can alter the corrosion reaction. Seemingly identical environmental conditions from one day to another, from one laboratory or plant to another, and so forth, can give rise to widely differing results. Those desiring a more detailed review of the subject are directed to the works of Pourbaix, Edeleanu, and other studies referred to in their publications.

The test to generate a CBD is generally as follows. At a rapid scan rate of about 50 V/h, the clean specimen is cathodically charged (polarized) starting at an electronegative position (with respect to SCE) that will produce a current density of 10^4 μA/cm^2 (nickel, chromium, and iron alloys in aggressive environments) and proceed in a noble (positive) direction. After completing the cathodic curve, proceed anodically until the current density reaches 10^3 μA/cm^2. The scan direction is reversed and potentials/currents recorded back to the starting point. The potentiostat is then shut off. The freely corroding potential (FCP), also referred to as the open circuit potential (OCP), is recorded after 10 min or when it is stable; that is, when the potential value remains constant. A third cathodic polarization curve is then generated by scanning from the corrosion potential in the negative direction to iron, again at a scan rate of 50 V/h. As noted earlier, this diagram can be produced in about 15 min; see Fig. 28-11.

The CBD diagram can provide various kinds of information about the performance of an alloy/medium system. The technique can be used for a direct calculation of the corrosion rate as well as for indicating the conditions of passivity and tendency of the metal to suffer local pitting and crevice attack.

Corrosion Rate by CBD Somewhat similarly to the Tafel extrapolation method, the corrosion rate is found by intersecting the extrapolation of the linear portion of the second cathodic curve with the equilibrium stable corrosion potential. The intersection corrosion current is converted to a corrosion rate (mils penetration per year [mpy], 0.001 in/y) by use of a conversion factor (based upon Faraday's law, the electrochemical equivalent of the metal, its valence and gram atomic weight). For 13 alloys, this conversion factor ranges from 0.42 for nickel to 0.67 for Hastelloy B or C. For a quick determination, 0.5 is used for most Fe, Cr, Ni, Mo, and Co alloy studies. Generally, the accuracy of the corrosion rate calculation is dependent upon the degree of linearity of the second cathodic curve; when it is less than 0.5 decade long, it becomes more difficult to extrapolate accurately. Obviously, the longer the better.

Expected Order of Magnitude of Corrosion by CBD The third cathodic curve will generally fall between the first two, or the first and third will coincide and fall positive to the second curve. These two curve configurations are only valid relationships for the projection of accurate corrosion rates. When, however, the second or third curve falls positive to the other two curves, a very high corrosion rate may be indicated. Another possibility is that the second or third curve in this positive position is not controlling corrosion because of surface films and so forth.

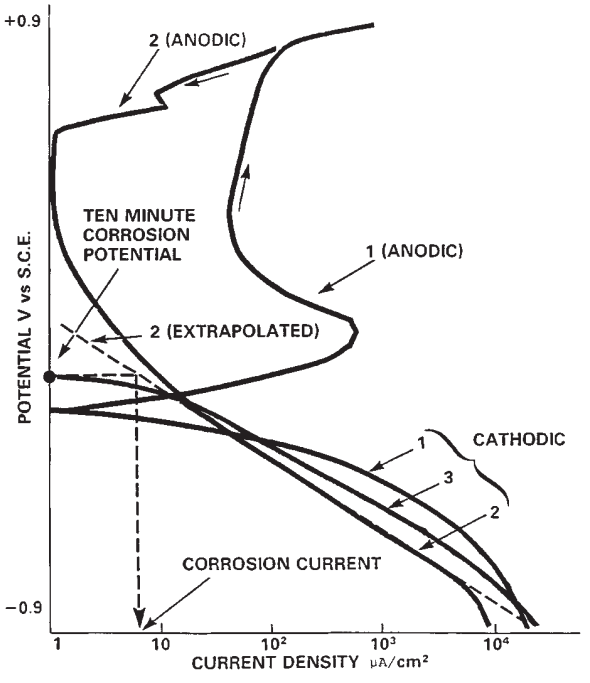


FIG. 28-11 Corrosion behavior diagram (CBD).

Spontaneous Passivation The anodic nose of the first curve describes the primary passive potential E_{pp} and critical anodic current density (the transition from active to passive corrosion). If the initial active/passive transition is 10^3 μA/cm^2 or less, the alloy will spontaneously passivate in the presence of oxygen or any strong oxidizing agent.

Anodic Protection On the reverse anodic scan there will be a low current region (LCR) in the passive range. The passive potential range of the LCR is generally much narrower than the passive region seen on a forward slow scan. In anodic protection (AP) work the midpoint of the LCR potential is the preferred design range. This factor was verified for sulfuric acid in our laboratory and field studies.

Pitting and Crevice Corrosion The general literature for predicting pitting tendency with the slow scan reviews the use of the reverse scan: If a hysteresis loop develops that comes back to the repassivation potential E_{repass} below the FCP (E_{corr}) the alloy will pit at crevices, when the value of the repassivation potential, identified by the return of the hysteresis loop, is above the FCP (E_{corr}), the pits will tend to grow. These rules of thumb have been expanded for rapid-scan.

1. If E_{corr} is equal to or greater than the pitting potential E_{pit}, both pitting and crevice-type attack are likely to occur on the specimen in an immersion test.
2. If E_{corr} is less than E_{pit}, pitting-type attack of the specimen is unlikely in an immersion test.
3. If the repassivation potential E_{repass} is greater than E_{corr}, crevice-type attack is possible in an immersion test.
4. If E_{corr} is equal to or larger than E_{repass}, crevice-type attack is probably in an immersion test.
5. If no E_{pit} can be determined, but cathodic Curves 1 and 2 cross at E_x forming a hysteresis loop, crevice-type attack during the rapid scan is indicated.
6. If E_x is equal to or greater than E_{pit}, pitting-type attack will be predominant during the rapid-scan test.
7. If E_{pit} is equal to or greater than E_x plus 100 mV, crevice-type attack is indicated during the rapid-scan test.
8. If the plot of Curve 1 continues from E_{pit} with a large increase in current density versus a small increase in voltage, the test specimen will suffer vigorous local attack during the rapid-scan test.
9. If the Curve 1, positive with respect to the value of E_{pit}, plots with a small increase in current density per large increase in voltage, the test specimen in the rapid-scan test will suffer only mild local attack (ASTM G31).

Scan Rates: Advantages versus Disadvantages As to the question of disadvantages of using the rapid-scan CBD, we believe it is more a case of looking to the limitations of the various benefits. In many of the places where these limitations to the use of the CBD show themselves, where the limitation provides information, for example, the corrosion rate will be too high, and so forth. Only in the case of interpretation of unstable active/passive conditions do we see the results of the rapid scan as a possible weakness of the technique (but it is not handled any better by other techniques). When the FCP is noble (positive) to the primary passive potential E_{pp}, the alloy is passive; when the FCP is active (negative) to the E_{pp}, the alloy will corrode in the active state; and when the FCP is only slightly more noble (positive) than the E_{pp}, the alloy could show active/passive tendencies. When the FCP oscillates and will not stabilize, the potential should be plotted against time. The alloy will probably not be resistant without AP but in these latter two cases, the CBD does not tell for sure.

Logic Sequence Diagram In order to expedite the interpretation of the 50.0-V/h anodic polarization data, three logic sequence diagrams (LSDs) were constructed (Figs. 28-12 through 28-14). These diagrams can be linked to each other to provide a more complete analysis of behavior if necessary. These LSDs contain benchmark values that have been derived from conducting more than 10,000 potentiodynamic experiments at scan rates of either 50.0 or 60.0 V/h.

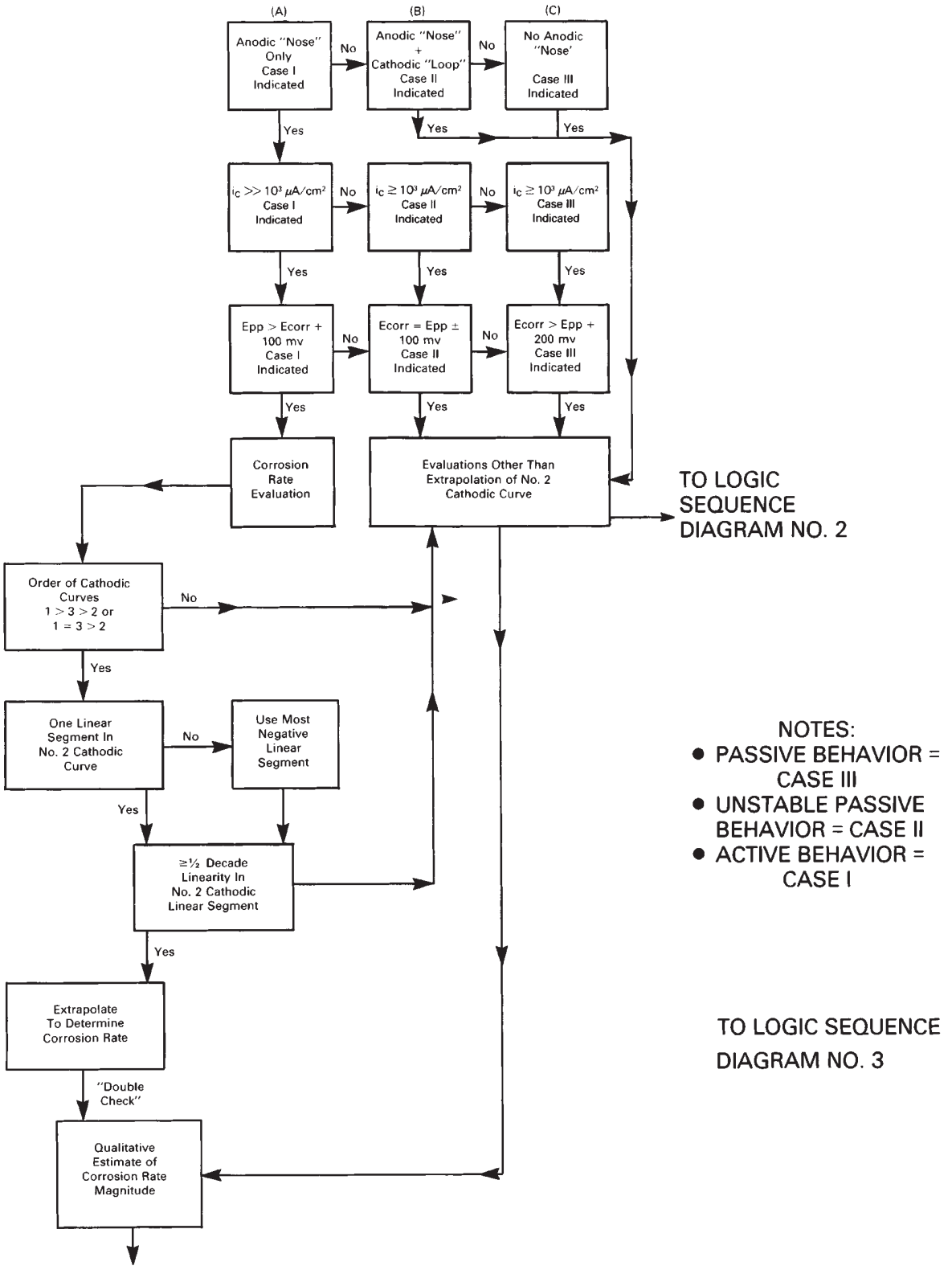


FIG. 28-12 Logic sequence Diagram 1 used to determine behavior type (Case 1, 2, and 3) and corrosion rate from a CBD.

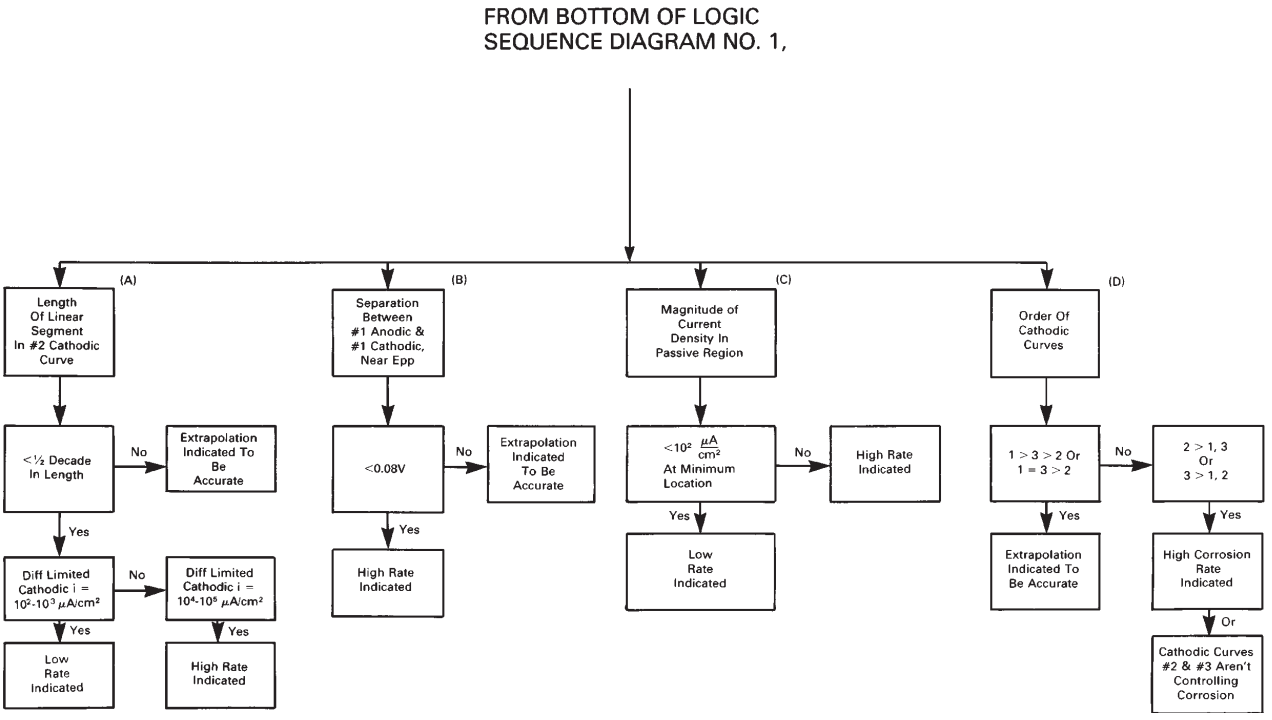


FIG. 28-13 Logic sequence Diagram 2 used to evaluate localized corrosion resistance from a CBD.

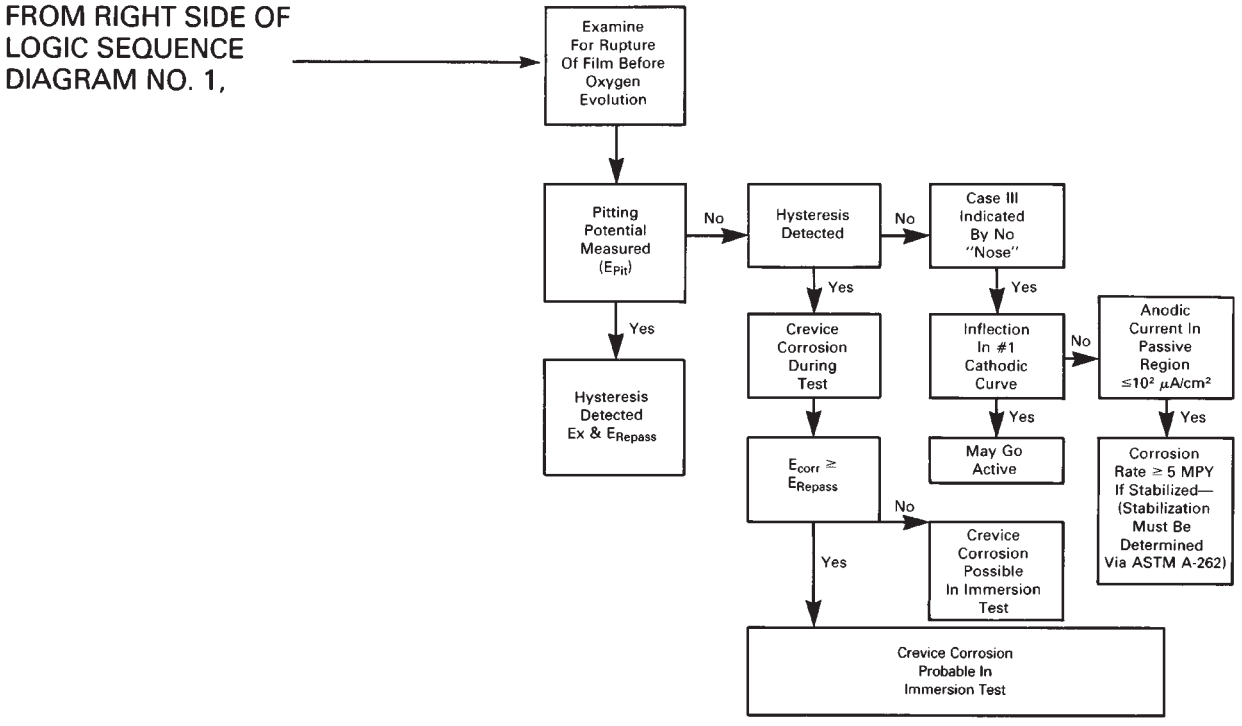


FIG. 28-14 Logic sequence Diagram 3 used to qualitatively evaluate the degree of corrosion for systems that cannot be evaluated by extrapolation of the cathodic polarization Curve 2 from a CBD.

Crevice Corrosion Prediction The most common type of localized corrosion is the occluded mode crevice corrosion. Pitting can, in effect, be considered a self-formed crevice. A crevice must be wide enough to permit liquid entry, but sufficiently narrow to maintain a stagnant zone. It is nearly impossible to build equipment without mechanical crevices; on a microlevel, scratches can be sufficient crevices to initiate or propagate corrosion in some metal/environment systems. The conditions in a crevice can, with time, become a different and much more aggressive environment than those on a nearby, clean, open surface. Crevices may also be created by factors foreign to the original system design, such as deposits, corrosion products, and so forth. In many studies, it is important to know or to be able to evaluate the crevice corrosion sensitivity of a metal to a specific environment and to be able to monitor a system for predictive maintenance.

Historically, the immersion test technique involved the use of a crevice created by two metal test specimens clamped together or a metal specimen in contact with an inert plastic or ceramic. The Materials Technology Institute of the Chemical Process Industries, Inc. (MTI) funded a study that resulted in an electrochemical cell to monitor crevice corrosion. It consists of a prepared crevice containing an anode that is connected through a zero-resistance ammeter to a freely exposed cathode. A string bridge provides a solution path that is attached externally to the cell. The electrochemical cell is shown in Fig. 28-15. A continuous, semiquantitative, real-time indication of crevice corrosion is provided by the magnitude of the current flowing between an anode and a cathode, and a qualitative signal is provided by shifts in electrode potential. Both the cell current and electrode potential produced by the test correlate well with the initiation and propagation of crevice corrosion. During development of the MTI test technique, results were compared with crevice corrosion produced by a grooved TFE Teflon® plastic disk sandwich-type crevice cell. In nearly every instance, corrosion damage on the anode was similar in severity to that produced by the sandwich-type cell.

Velocity For corrosion to occur, an environment must be brought into contact with the metal surface and the metal atoms or ions must be allowed to be transported away. Therefore, the rate of transport of the environment with respect to a metal surface is a major factor in the corrosion system. Changes in velocity may increase or decrease attack depending on its effect involved. A varying quantity of dissolved gas may be brought in contact with the metal, or velocity changes may alter diffusion or transfer of ions by changing the thickness of the boundary layer at the surface. The boundary layer, which is not stagnant, moves except where it touches the surface. Many metals depend upon the development of a protective surface for their corrosion resistance. This may consist of an oxide film, a corrosion product, an adsorbed film of gas, or other surface phenomena. The removal of these surfaces by effect of the fluid velocity exposes fresh metal, and as a result, the corrosion reaction may proceed at an increasing rate. In these systems, corrosion might be minimal until a so-called **critical velocity** is attained where the protective surface is damaged or removed and the velocity is too high for a stable film to reform. Above this critical velocity, the corrosion may increase rapidly.

The NACE Landrum Wheel velocity test, originally TM0270-72, is typical of several mechanical-action immersion test methods to evaluate the effects of corrosion. Unfortunately, these laboratory simulation techniques did not consider the fluid mechanics of the environment or metal interface, and service experience very seldom supports the test predictions. A rotating cylinder within a cylinder electrode test system has been developed that operates under a defined hydrodynamics relationship (Figs. 28-16 and 28-17). The assumption is that if the rotating electrode operates at a shear stress comparable to that in plant geometry, the mechanism in the plant geometry may be modeled in the laboratory. Once the mechanism is defined, the appropriate relationship between fluid flow rate and corrosion rate in the plant equipment as defined by the mechanism can be used to predict the expected corrosion rate. If fluid velocity does affect the corrosion rate, the degree of mass transfer control, if that is the controlling mechanism (as opposed to activation control), can be estimated. Conventional potentiodynamic polarization scans are conducted as described previously. In other cases, the corrosion potential can be monitored at a constant velocity until steady state is attained. While the value of the final corrosion potential is virtually independent of velocity, the time to reach steady state may be dependent on velocity. The mass-transfer control of the corrosion potential can be proportional to the velocity raised to its appropriate exponent. The rate of breakdown of a passive film is velocity-sensitive.

Environmental Cracking The problem of environmental cracking of metals and their alloys is very important. Of all the failure mechanism tests, the test for stress corrosion cracking (SCC) is the most illusive. Stress corrosion is the acceleration of the rate of corrosion damage by static stress. SCC, the limiting case, is the spontaneous cracking that may result from combined effects of stress and corrosion. It is important to differentiate clearly between **stress corrosion cracking** and **stress accelerated corrosion.** Stress corrosion cracking is considered to be limited to cases in which no significant corrosion damage occurs in the absence of a corrosive environment. The material exhibits normal mechanical behavior under the influence of stress; before the development of a stress corrosion

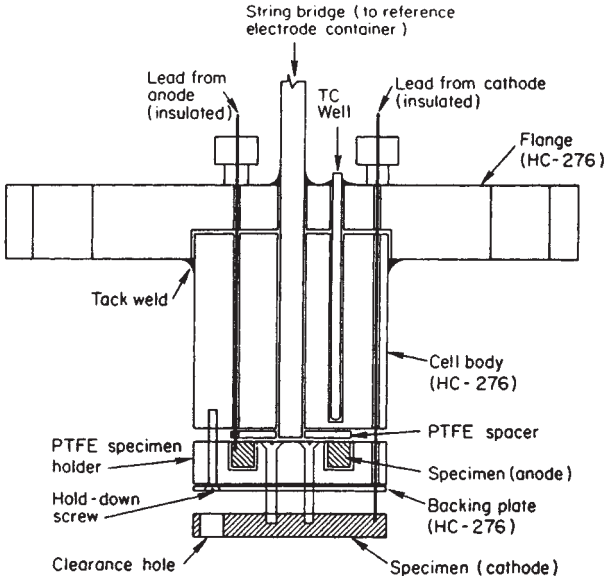


FIG. 28-15 Schematic diagram of the electrochemical cell used for crevice corrosion testing. Not shown are three hold-down screws, gas inlet tube, and external thermocouple tube.

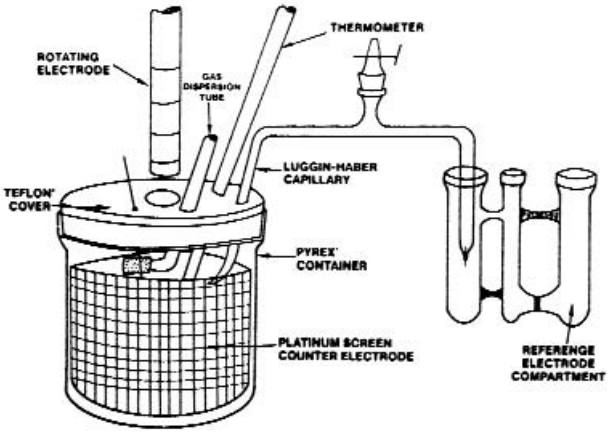


FIG. 28-16 Rotating cylinder electrode apparatus.

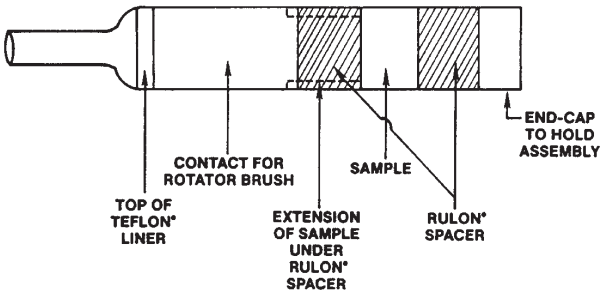


FIG. 28-17 Inner rotating cylinder used in laboratory apparatus of Fig. 28-16.

crack, there is little deterioration of strength and ductility. Stress corrosion cracking is the case of an interaction between chemical reaction and mechanical forces that results in structural failure that otherwise would not occur. SCC is a type of brittle fracture of a normally ductile material by the interaction between specific environments and mechanical forces, for example, tensile stress. Stress corrosion cracking is an incompletely understood corrosion phenomenon. Much research activity (aimed mostly at mechanisms) plus practical experience has allowed crude empirical guidelines, but these contain a large element of uncertainty. No single chemical, structural, or electrochemical test method has been found to respond with enough consistent reproducibility to known crack-causing environmental/stressed metal systems to justify a high confidence level.

As was cited in the case of immersion testing, most SCC test work is accomplished using mechanical, nonelectrochemical methods. It has been estimated that 90 percent of all SCC testing is handled by one of the following methods: (1) constant strain, (2) constant load, or (3) precracked specimens. Prestressed samples, such as are shown in Fig. 28-18, have been used for laboratory and field SCC testing. The variable observed is "time to failure or visible cracking." Unfortunately, such tests do not provide acceleration of failure.

Since SCC frequently shows a fairly long induction period (months to years), such tests must be conducted for very long periods before reliable conclusions can be drawn.

In the constant-strain method, the specimen is stretched or bent to a fixed position at the start of the test. The most common shape of the specimens used for constant-strain testing is the U-bend, hairpin, or horseshoe type. A bolt is placed through holes in the legs of the specimen, and it is loaded by tightening a nut on the bolt. In some cases, the stress may be reduced during the test as a result of creep. In the constant-load test the specimen is supported horizontally at each end and is loaded vertically downward at one or two points and has maximum stress over a substantial length or area of the specimen. The load applied is a predetermined, fixed dead weight. Specimens used in either of these tests may be precracked to assign a stress level or a desired location for fracture to occur or both as is used in fracture mechanics studies. These tensile-stressed specimens are then exposed in situ to the environment of study.

Slow Strain-Rate Test In its present state of development, the results from slow strain-rate tests (SSRT) with electrochemical monitoring are not always completely definitive; but, for a short-term test, they do provide considerable useful SCC information. Work in our laboratory shows that the SSRT with electrochemical monitoring and the U-bend tests are essentially equivalent in sensitivity in finding SCC. The SSRT is more versatile and faster, providing both mechanical and electrochemical feedback during testing.

The SSRT is a test technique where a tension specimen is slowly loaded in a test frame to failure under prescribed test conditions. The normal test extension rates are from 2.54×10^{-7} to 2.54×10^{-10} m/s (10^{-5} to 10^{-8} in/s). Failure times are usually 1 to 10 days. The failure mode will be either SCC or tensile overload, sometimes accelerated by corrosion. An advantage behind the SSRT, compared to constant-strain tests, is that the protective surface film is thought to be ruptured mechanically during the test, thus giving SCC an opportunity to progress. To aid in the selection of the value of the potential at which the metal is most sensitive to SCC that can be applied to accelerate SSRT, potentiodynamic polarization scans are conducted as described previously. It is common for the potential to be monitored during the conduct of the SSRT. The strain rates that generate SCC in various metals are reported in the literature. There are several disadvantages to the SSRT. First, indications of failure are not generally observed until the tension specimen is plasticly stressed, sometimes significantly, above the yield strength of the metal. Such high-stressed conditions can be an order of magnitude higher than the intended operating stress conditions. Second, crack initiation must occur fairly rapidly to have sufficient crack growth that can be detected using the SSRT. The occurrence of SCC in metals requiring long initiation times may go undetected.

Modulus Measurements Another SCC test technique is the use of changes of modulus as a measure of the damping capacity of a metal. It is known that a sample of a given test material containing cracks will have a lower effective modulus than does a sample of identical material free of cracks. The technique provides a rapid and reliable evaluation of the susceptibility of a sample material to SCC in a specific environment. The so-called internal friction test concept can also be used to detect and probe nucleation and progress of cracking and the mechanisms controlling it.

The Young's modulus of the specimen is determined by accurately measuring its resonant frequency while driving it in a standing longi-

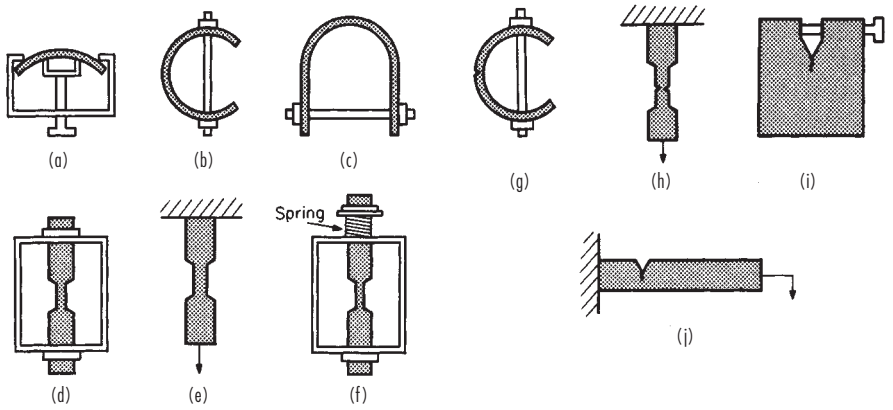


FIG. 28-18 Specimens for stress-corrosion tests. (*a*) Bent beam. (*b*) C ring. (*c*) U bend. (*d*) Tensile. (*e*) Tensile. (*f*) Tensile. (*g*) Notched C ring. (*h*) Notched tensile. (*i*) Precracked, wedge open-loading type. (*j*) Precracked, cantilever beam. [Chem. Eng., ***78,*** *159 (Sept. 20 1971).*]

tudinal wave configuration. A Marx composite piezoelectric oscillator is used to drive the specimen at a resonant frequency. The specimen is designed to permit measurements while undergoing applied stress and while exposed to an environmental test solution. The specimens are three half-wavelengths long; the gripping nodes and solution cup are silver-soldered on at displacement nodes, so they do not interfere with the standing wave (Fig. 28-19). As discussed for SSRT, potentiodynamic polarization scans are conducted to determine the potential that can be applied to accelerate the test procedure. Again, the potential can be monitored during a retest, as is the acoustic emission (AE) as an indicator of nucleation and progress of cracking.

Conjunctive Use of Slow- and Rapid-Scan Polarization The use of the methods discussed in the preceding requires a knowledge of the likely potential range for SCC to occur. Potentiodynamic polarization curves can be used to predict those SCC-sensitive potential ranges. The technique involves conducting both slow- and rapid-scan sweeps in the anodic direction of a range of potentials. Comparison of the two curves will indicate any ranges of potential within which high anodic activity in the film-free condition reduces to insignificant activity when the time requirements for film formation are met. This should indicate the range of potentials within which SCC is likely. Most of the SCC theories presently in vogue predict these domains of behavior to be between the primary passive potential and the onset of passivity. This technique shortens the search for that SCC potential.

Separated Anode/Cathode Realizing, as noted in the preceding, that localized corrosion is usually active to the surrounding metal surface, a stress specimen with a limited area exposed to the test solution (the anode) is electrically connected to an unstressed specimen (the cathode). A potentiostat, used as a zero-resistance ammeter, is placed between the specimens for monitoring the galvanic current. It is possible to approximately correlate the galvanic current I_g and potential to crack initiation and propagation, and, eventually, catastrophic failure. By this arrangement, the galvanic current I_g is independent of the cathode area. In other words, the potential of the anode follows the corrosion potential of the cathode during the test. The SSRT apparatus discussed previously may be used for tensile loading.

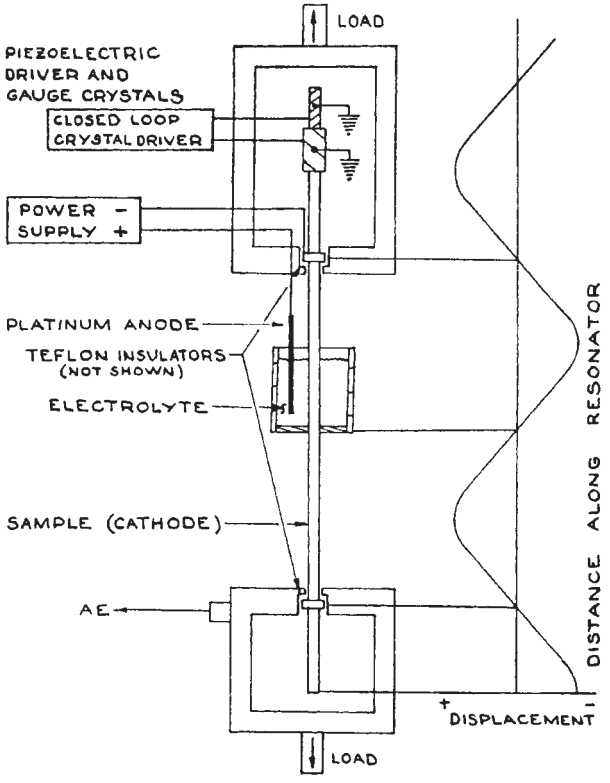


FIG. 28-19 Equipment for measuring internal friction (modulus) changes during in situ tensile exposure of a metal in a corrosive environment.

Fracture Mechanics Methods These have proved very useful for defining the minimum stress intensity K_{ISCC} at which stress corrosion cracking of high-strength, low-ductility alloys occurs. They have so far been less successful when applied to high-ductility alloys, which are extensively used in the chemical-process industries.

Work on these and other new techniques continues, and it is hoped that a truly reliable, accelerated test or tests will be defined.

Electrochemical Impedance Spectroscopy (EIS) and AC Impedance* Many direct-current test techniques assess the overall corrosion process occurring at a metal surface, but treat the metal/solution interface as if it were a pure resistor. Problems of accuracy and reproducibility frequently encountered in the application of direct-current methods have led to increasing use of electrochemical impedance spectroscopy (EIS).

Electrode surfaces in electrolytes generally possess a surface charge that is balanced by an ion accumulation in the adjacent solution, thus making the system electrically neutral. The first component is a double layer created by a charge difference between the electrode surface and the adjacent molecular layer in the fluid. Electrode surfaces may behave at any given frequency as a network of resistive and capacitive elements from which an electrical impedance may be measured and analyzed.

The application of an impressed alternating current on a metal specimen can generate information on the state of the surface of the specimen. The corrosion behavior of the surface of an electrode is related to the way in which that surface responds to this electrochemical circuit. The AC impedance technique involves the application of a small sinusoidal voltage across this circuit. The frequency of that alternating signal is varied. The voltage and current response of the system are measured.

The so-called white-noise analysis by the Fast Fourier transform technique (FFT) is another viable method. The entire spectrum can be derived from one signal. The impedance components thus generated are plotted on either a Nyquist (real versus imaginary) or Bode (log real versus log frequency plus log phase angle versus log frequency) plot. These data are analyzed by computer; they can be used to determine the polarization resistance and, thus, the corrosion rate if Tafel slopes are known. It is also thought that the technique can be used to monitor corrosion by examining the real resistance at high and low frequency and by assuming the difference is the polarization resistance. This can be done in low- and high-conductivity environments. Systems prone to suffer localized corrosion have been proposed to be analyzed by AC impedance and should aid in determining the optimum scan rate for potentiodynamic scans.

The use of impedance electrochemical techniques to study corrosion mechanisms and to determine corrosion rates is an emerging technology. Electrode impedance measurements have not been widely used, largely because of the sophisticated electrical equipment required to make these measurements. Recent advantages in microelectronics and computers has moved this technique almost overnight from being an academic experimental investigation of the concept itself to one of shelf-item commercial hardware and computer software, available to industrial corrosion laboratories.

Use and Limitations of Electrochemical Techniques A major caution must be noted as to the general, indiscriminate use of all electrochemical tests, especially the use of AC and EIS test techniques, for the study of corrosion systems. AC and EIS techniques are applicable for the evaluation of very thin films or deposits that are uniform, constant, and stable—for example, thin-film protective coatings. Sometimes, researchers do not recognize the dynamic nature of some passive films, corrosion products, or deposits from other sources; nor do they even consider the *possibility of a change* in the surface conditions during the course of their experiment. As an example, it is note-

* Excerpted from papers by Oliver W. Siebert, courtesy of NACE International and ASTM.

worthy that this is a *major* potential problem in the electrochemical evaluation of microbiological corrosion (MIC).

MIC depends on the complex structure of corrosion products and passive films on metal surfaces as well as on the structure of the biofilm. Unfortunately, electrochemical methods have sometimes been used in complex electrolytes, such as microbiological culture media, where the characteristics and properties of passive films and MIC deposits are *quite active* and not fully understood. It must be kept in mind that microbial colonization of passive metals can drastically change their resistance to film breakdown by causing *localized* changes in the type, concentration, and thickness of anions, pH, oxygen gradients, and inhibitor levels at the metal surface during the course of a normal test; viable single-cell microorganisms divide at an exponential rate. These changes can be expected to result in important modifications in the electrochemical behavior of the metal and, accordingly, in the electrochemical parameter measured in laboratory experiments.

Warnings are noted in the literature to be careful in the *interpretation* of data from electrochemical techniques applied to systems in which complex and often poorly understood effects are derived from surfaces which contain *active* or *viable* organisms, and so forth. Rather, it is even more important to not use such test protocol unless the investigator fully understands both the corrosion mechanism and the test technique being considered—and their interrelationship.

CORROSION TESTING: PLANT TESTS

It is not always practical or convenient to investigate corrosion problems in the laboratory. In many instances, it is difficult to discover just what the conditions of service are and to reproduce them exactly. This is especially true with processes involving changes in the composition and other characteristics of the solutions as the process is carried out, as, for example, in evaporation, distillation, polymerization, sulfonation, or synthesis.

With many natural substances also, the exact nature of the corrosive is uncertain and is subject to changes not readily controlled in the laboratory. In other cases, the corrosiveness of the solution may be influenced greatly by or even may be due principally to a constituent present in such minute proportions that the mass available in the limited volume of corrosive solution that could be used in a laboratory setup would be exhausted by the corrosion reaction early in the test, and consequently the results over a longer period of time would be misleading.

Another difficulty sometimes encountered in laboratory tests is that contamination of the testing solution by corrosion products may change its corrosive nature to an appreciable extent.

In such cases, it is usually preferable to carry out the corrosion-testing program by exposing specimens in operating equipment under **actual conditions of service.** This procedure has the additional advantages that it is possible to test a large number of specimens at the same time and that little technical supervision is required.

In certain cases, it is necessary to choose materials for equipment to be used in a process developed in the laboratory and not yet in operation on a plant scale. Under such circumstances, it is obviously impossible to make plant tests. A good procedure in such cases is to construct a pilot plant, using either the cheapest materials available or some other materials selected on the basis of past experience or of laboratory tests. While the pilot plant is being operated to check on the process itself, specimens can be exposed in the operating equipment as a guide to the choice of materials for the large-scale plant or as a means of confirming the suitability of the materials chosen for the pilot plant.

Test Specimens In carrying out plant tests it is necessary to install the test specimens so that they will not come into contact with other metals and alloys; this avoids having their normal behavior disturbed by galvanic effects. It is also desirable to protect the specimens from possible mechanical damage.

There is no single standard size or shape for corrosion-test coupons. They usually weigh from 10 to 50 g and preferably have a large surface-to-mass ratio. Disks 40 mm (1½ in) in diameter by 3.2 mm (⅛ in) thick and similarly dimensioned square and rectangular coupons are the most common. Surface preparation varies with the aim of the test, but machine grinding of surfaces or polishing with a No. 120 grit is common. Samples should not have sheared edges, should be clean (no heat-treatment scale remaining unless this is specifically part of the test), and should be identified by stamping. See Fig. 28-20 for a typical plant test assembly.

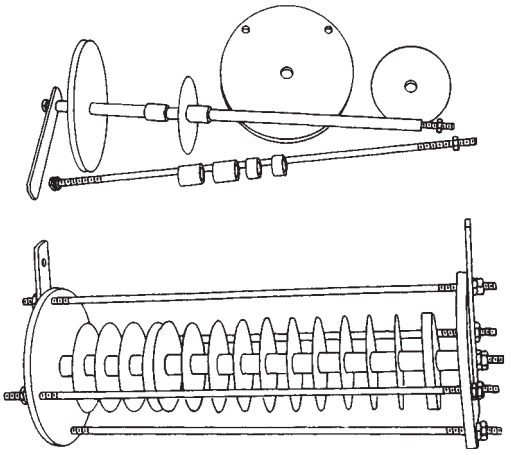


FIG. 28-20 Assembly of a corrosion-test spool and specimens. (*Mantell, ed.,* Engineering Materials Handbook, *McGraw-Hill, New York, 1958.*)

The choice of materials from which to make the holder is important. Materials must be durable enough to ensure satisfactory completion of the test. It is good practice to select very resistant materials for the test assembly. Insulating materials used are plastics, porcelain, Teflon, and glass. A phenolic plastic answers most purposes; its principal limitations are unsuitability for use at temperatures over 150°C (300°F) and lack of adequate resistance to concentrated alkalies.

The method of supporting the specimen holder during the test period is important. The preferred position is with the long axis of the holder horizontal, thus avoiding dripping of corrosion products from one specimen to another. The holder must be located so as to cover the conditions of exposure to be studied. It may have to be submerged, or exposed only to the vapors, or located at liquid level, or holders may be called for at all three locations. Various means have been utilized for supporting the holders in liquids or in vapors. The simplest is to suspend the holder by means of a heavy wire or light metal chain. Holders have been strung between heating coils, clamped to agitator shafts, welded to evaporator tube sheets, and so on. The best method is to use test racks.

In a few special cases, the standard "spool-type" specimen holder is not applicable and a suitable special test method must be devised to apply to the corrosion conditions being studied.

For conducting tests in **pipe lines** of 75-mm (3-in) diameter or larger, a spool holder as shown in Fig. 28-21, which employs the same disk-type specimens used on the standard spool holder, has been used. This frame is so designed that it may be placed in a pipe line in any position without permitting the disk specimens to touch the wall of the pipe. As with the strip-type holder, this assembly does not materially interfere with the fluid through the pipe and permits the study of corrosion effects prevailing in the pipe line.

Another way to study corrosion in pipe lines is to install in the line short sections of pipe of the materials to be tested. These test sections should be insulated from each other and from the rest of the piping system by means of nonmetallic couplings. It is also good practice to provide insulating gaskets between the ends of the pipe specimens where they meet inside the couplings. Such joints may be sealed with various types of dope or cement. It is desirable in such cases to paint the outside of the specimens so as to confine corrosion to the inner surface.

It is occasionally desirable to expose corrosion-test specimens in operating equipment without the use of specimen holders of the type

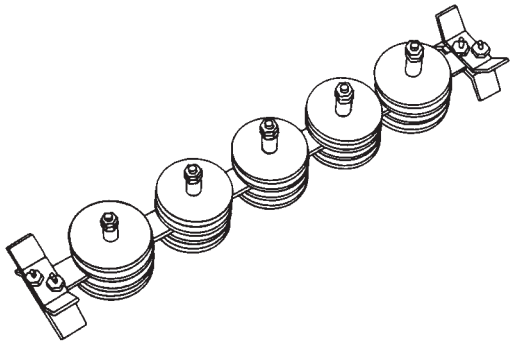


FIG. 28-21 Spool-type specimen holder for use in 3-in-diameter or larger pipe. (*Mantell, ed.,* Engineering Materials Handbook, *McGraw-Hill, New York, 1958.*)

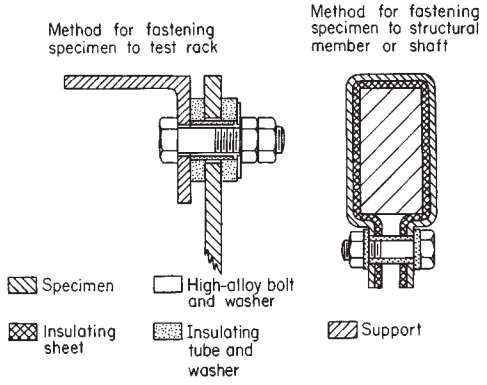


FIG. 28-22 Methods for attaching specimens to test racks and to parts of moving equipment. (*Mantell, ed.,* Engineering Materials Handbook, *McGraw-Hill, New York, 1958.*)

described. This can be accomplished by attaching specimens directly to some part of the operating equipment and by providing the necessary insulation against galvanic effects as shown in Fig. 28-22. The suggested method of attaching specimens to racks has been found to be very suitable in connection with the exposure of specimens to corrosion in seawater.

Test Results The methods of cleaning specimens and evaluating results after plant corrosion tests are identical to those described earlier for laboratory tests.

Electrochemical On-Line Corrosion Monitoring* On-line corrosion monitoring is used to evaluate the status of equipment and piping in chemical process industries (CPI) plants. These monitoring methods are based on electrochemical techniques. To use on-line monitoring effectively, the engineer needs to understand the underlying electrochemical test methods to be employed. This section covers many of these test methods and their applications as well as a review of potential problems encountered with such test instruments and how to overcome or avoid these difficulties.

Most Common Types of Probes There are three most common types of corrosion monitoring probes used. Other types of probes are used, but in smaller numbers.

1. *Weight loss probes.* Coupons for measuring weight loss are still the primary type of probe in use. These may be as simple as samples of the process plant materials which have been fitted with electrical connections and readouts to determine intervals for retrieval and weighing, to commercially available coupons of specified material, geometry, stress condition, and other factors, ready to be mounted on specially designed supports at critical points in the process. Coupons can be permanently installed prior to plant start-up or during a shutdown. This type of permanent installation requires a plant shutdown for probe retrieval as well. Shutdown can be avoided by installing the probe in a bypass.

2. *Electrical resistance probes.* These probes are the next most common type of corrosion probes after coupons. This type of probe measures changes in the electrical resistance as a thin strip of metal gets thinner with ongoing corrosion. As the metal gets thinner, its resistance increases. This technique was developed in the 1950s by Dravinieks and Cataldi and has undergone many improvements since then.

3. *Linear polarization resistance probes.* LPR probes are more recent in origin, and are steadily gaining in use. These probes work on a principle outlined in an ASTM guide on making polarization resistance measurements, providing instantaneous corrosion rate measurements (G59, "Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements").

LPR probes measure the electrochemical corrosion mechanism involved in the interaction of the metal with the electrolyte. To measure linear polarization resistance R_p, Ω/cm^2, the following assumptions must be made:

- The corrosion rate is uniform.
- There is only cathodic and one anodic reaction.
- The corrosion potential is not near the oxidation/reduction potential for either reaction.

When these conditions are met, the current density associated with a small polarization of the metal (less than +10 mV) is directly proportional to the corrosion rate of the metal.

Multiinformational Probes Corrosion probes can provide more information than just corrosion rate. The next three types of probes yield information about the type of corrosion, the kinetics of the corrosion reaction, as well as the local corrosion rate.

Electrochemical impedance spectroscopy, AC probes. EIS, although around since the 1960s, has primarily been a laboratory technique. Commercially available probes and monitoring systems that measure EIS are becoming more widely used, especially in plants that have on-staff corrosion experts to interpret the data or to train plant personnel to do so.

In EIS, a potential is applied across a corroding metal in solution, causing current to flow. The amount of current depends upon the corrosion reaction on the metal surface and the flow of ions in solution. If the potential is applied as a sine wave, it will cause harmonics of the current output. The relationship between the applied potential and current output is the impedance, which is analogous to resistance in a DC circuit.

Since the potential and current are sinusoidal, the impedance has a magnitude and a phase, which can be represented as a vector. A sinusoidal potential or current can be pictured as a rotating vector. For standard AC current, the rotation is at a constant angular velocity of 60 Hz.

The voltage can also be pictured as a rotating vector with its own amplitude and frequency. Both current and potential can be represented as having real (observed) and imaginary (not observed) components.

In making electrochemical impedance measurements, one vector is examined, using the others as the frame of reference. The voltage vector is divided by the current vector, as in Ohm's law. Electrochemical impedance measures the impedance of an electrochemical system and then mathematically models the response using simple circuit elements such as resistors, capacitors, and inductors. In some cases, the circuit elements are used to yield information about the kinetics of the corrosion process.

Polarization probes. Polarization methods other than LPR are also of use in process control and corrosion analysis, but only a few systems are offered commercially. These systems use such polarization techniques as galvanodynamic or potentiodynamic, potentiostatic or galvanostatic, potentiostaircase or galvanostaircase, or cyclic polarization methods. Some systems involving these techniques are, in fact, used regularly in processing plants. These methods are used in situ or

* Excerpted from papers by Ann Chidester Van Orden and Oliver W. Siebert, courtesy of NACE International and Oliver W. Siebert, courtesy of ASTM.

in the laboratory to measure corrosion. Polarization probes have been successful in reducing corrosion-related failures in chemical plants.

Polarization probes rely on the relationship of the applied potential to the output current per unit area (current density). The slope of applied potential versus current density, extrapolated through the origin, yields the polarization resistance R_p, which can be related to the corrosion rate.

There are several methods for relating the corrosion current, the applied potential, and the polarization resistance. These methods involve various ways of stepping or ramping either the potential or current. Also, a constant value of potential or current can be applied.

Electrochemical noise monitoring probes. Electrochemical noise monitoring is probably the newest of these methods. The method characterizes the naturally occurring fluctuations in current and potential due to the electrochemical kinetics and the mechanism of the corroding metal interface. Measurements are taken without perturbing the interface by applying a potential or current to it. In this way, electrochemical processes are not interrupted and the system is measured without being disturbed. Methods including signal processing and mathematical transformation are used to provide information on the reaction kinetics at the surface and the corrosion rate.

This technique, originally discovered in the 1960s, remained a laboratory technique until recently, when some manufacturers began producing commercial devices. There are a few cases where electrochemical noise is being used in process-plant-type environments, and an ASTM committee has been formed to look at standardization of this technique. However, in general it remains a laboratory method with great potential for on-line monitoring.

Indirect Probes Some types of probes do not measure corrosion directly, but yield measurements that also are useful in detecting corrosion. Examples include:

Pressure probes. Pressure monitors or transducers may be of use in corrosion monitoring in environments where buildup of gases such as hydrogen or H_2S may contribute to corrosion.

Gas probes. The hydrogen patch probe allows users to determine the concentration of hydrogen in the system. This is an important measurement since hydrogen can foster corrosion. Detecting production of certain gases may give rise to process changes to eliminate or limit the gaseous effluent and, therefore, lower the possibility of corrosion caused by these gases.

pH probes. Monitoring the pH may also aid in the early detection of corrosion. The acidity or alkalinity of the environment is often one of the controllable parameters in corrosion. Monitoring of the pH can be combined with other corrosion measurements to provide additional data about process conditions and give another level of process control.

Ion probes. Determining the level of ions in solution also helps to control corrosion. An increase in concentration of specific ions can contribute to scale formation, which can lead to a corrosion-related failure. Ion-selective electrode measurements can be included, just as pH measurements can, along with other more typical corrosion measurements. Especially in a complete monitoring system, this can add information about the effect of these ions on the material of interest at the process plant conditions.

Microbially induced corrosion (MIC) probes. Devices are available to measure the amount of microbial activity in some environments. Microbially induced corrosion is known to be an actor in many corrosion-related problems in processing plants. The monitoring devices for MIC are limited in their range and, at present, are available only for a few specific environments. This is an exciting area for development of corrosion probes and monitoring systems.

Use of Corrosion Probes The major use of corrosion monitoring probes is to measure the corrosion rate in the plant or the field. In addition to corrosion-rate measurements, corrosion probes can be used to detect process upsets that may change the corrosion resistance of the equipment of interest. This is usually equally as important a measurement as corrosion rate since a change in the process conditions can lead to dramatic changes in the corrosion rate.

If the upset can be detected and dealt with in short order, the system can be protected. Some of the probes that measure parameters such as pH, ion content, and others are sensitive to process upsets and may give the fastest most complete information about such changes.

Monitoring can also be used to optimize the chemistry and level of corrosion inhibitors used. If too little inhibitor is used, enhanced corrosion can result and failure may follow. If too much is used, costs will increase without providing any additional protection. Optimization of the addition of inhibitor in terms of time, location in the process, and method of addition can also be evaluated through the use of carefully placed probes.

Another area where probes can be used effectively is in monitoring of deposits such as scale. One method of measurement is detecting specific ions that contribute to scale buildup or fouling; another is measuring the actual layers. Scale and fouling often devastate the corrosion resistance of a system, leading to a costly corrosion-related plant shutdown.

A final type of measurement is the detection of localized corrosion, such as pitting or crevice attack. Several corrosion-measuring probes can be used to detect localized corrosion. Some can detect localized corrosion instantaneously and others only its result. These types of corrosion may contribute little to the actual mass loss, but can be devastating to equipment and piping. Detection and measurement of localized corrosion is one of the areas with the greatest potential for the use of some of the newest electrochemically based corrosion monitoring probes.

Corrosion Rate Measurements Determining a corrosion rate from measured parameters (such as mass loss, current, or electrical potential) depends on converting the measurements into a corrosion rate by use of relationships such as Faraday's law.

Information on the process reaction conditions may be important to prolonging the lifetime of process equipment. Techniques such as EIS and potentiodynamic polarization can provide just such information without being tied to a specific corrosion-rate measurement.

This is also the case with methods that yield information on localized corrosion. The overall corrosion rate may be small when localized attack occurs, but failure due to perforation or loss of function may be the consequence of localized attack.

Measuring Corrosion Rate with Coupons Corrosion rate determined with typical coupon tests is an average value, averaged over the entire life of the test. Changes in the conditions under which the coupons are tested are averaged over the time the coupon is exposed. *Uniform attack is assumed to occur.* Converting measured values of loss of mass into an average corrosion rate has been covered extensively by many authors, and standard practices exist for determining corrosion rate.

Corrosion rates may vary during testing. Since the rate obtained from coupon testing is averaged over time, the frequency of sampling is important. Generally, measurements made over longer times are more valid. This is especially true for low corrosion rates, under 1 mil/y, mpy (0.001 in/y). When corrosion rates are this low, longer times should be used.

Factors may throw off these rates—these are outlined in ASTM G31, "Standard Practice for Laboratory Immersion Corrosion Testing of Metals." Coupon-type tests cannot be correlated with changing plant conditions that may dramatically affect process equipment lifetimes. Other methods must be used if more frequent measurements are desired or correlation with plant conditions are necessary.

A plot of mass loss versus time can provide information about changes in the conditions under which the test has been run. One example of such a plot comes from the ASTM Standard G96, "Standard Guide."

Heat Flux Tests Removable tube test heat exchangers find an ideal use in the field for monitoring heat flux (corrosion) conditions, NACE TMO286-94 (similar to laboratory test, Fig. 28-4, page 28-12).

The assumption of uniform corrosion is also at the heart of the measurements made by the electrical resistance (ER) probes. Again, ASTM Standard G96 outlines the method for using ER probes in plant equipment. These probes operate on the principle that the electrical resistance of a wire, strip, or tube of metal increases as its cross-sectional area decreases:

$$R = \frac{\rho L}{A}$$

where R = resistance, Ω
ρ = resistivity, Ω/cm
L = length, cm
A = cross-sectional area, cm^2

Usually, in practice, the resistance is measured as a ratio between the actual measuring element and a similar element protected from the corrosive environment (the reference), and is given by R_M/R_R where subscript M is for measured and R is for reference.

Measurements are recorded intermittently or continuously. Changes in the slope of the curve obtained thus yields the corrosion rate.

The initial measurement of electrical resistance must be made after considerable time. Phenomenological information has been determined based on the corrosion rate expected at what period of time to initiate readings of the electrical resistance. Since these values are based on experiential factors rather than on fundamental (so-called *first*) principles, correlation tables and lists of suggested thicknesses, compositions, and response times for usage of ER-type probes have developed over time, and these have been incorporated into the values read out of monitoring systems using the ER method.

Electrochemical Measurement of Corrosion Rate There is a link between electrochemical parameters and actual corrosion rates. Probes have been specifically designed to yield signals that will provide this information. LPR, ER, and EIS probes can give corrosion rates directly from electrochemical measurements. ASTM G102, "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements," tells how to obtain corrosion rates directly. Background on the approximations made in making use of the electrochemical measurements has been outlined by several authors.

ASTM G59, "Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements," provides instructions for the graphical plotting of data (from tests conducted using the above-noted ASTM Standard G103) as the linear potential versus current density, from which the polarization resistance can be found.

Measurements of polarization resistance R_p, given by LPR probes, can lead to measurement of the corrosion rate at a specific instant, since values of R_p are instantaneous.

To obtain the corrosion current I_{corr} from R_p, values for the anodic and cathodic slopes must be known or estimated. ASTM G59 provides an experimental procedure for measuring R_p. A discussion of the factors which may lead to errors in the values for R_p, and cases where R_p technique cannot be used, are covered by Mansfeld in "Polarization Resistance Measurements—Today's Status, Electrochemical Techniques for Corrosion Engineers" (NACE International, 1992).

Some data from corrosion-monitoring probes do not measure corrosion rate, but rather give other useful information about the system. For example, suppose conditions change dramatically during a process upset. An experienced corrosion engineer can examine the data and correlate it with the upset conditions. Such analysis can provide insight into the process and help to improve performance and extend equipment lifetime. Changes in simple parameters such as pH, ion content, and temperature may lead to detection of a process upset. Without careful analysis, process upsets can reduce the corrosion lifetime of equipment and even cause a system failure.

Analysis of biological activity does not automatically lead directly to a corrosion-rate measurement. However, with detection and correlation with process conditions, such information may also lead to improvements in the corrosion lifetime of the process equipment.

Evidence of localized corrosion can be obtained from polarization methods such as potentiodynamic polarization, EIS, and electrochemical noise measurements, which are particularly well suited to providing data on localized corrosion. When evidence of localized attack is obtained, the engineer needs to perform a careful analysis of the conditions that may lead to such attack. Correlation with process conditions can provide additional data about the susceptibility of the equipment to localized attack and can potentially help prevent failures due to pitting or crevice corrosion. Since pitting may have a delayed initiation phase, careful consideration of the cause of the localized attack is critical. Laboratory testing and involvement of an experienced corrosion engineer may be needed to understand the initiation of localized corrosion. Theoretical constructs such as Pourbaix diagrams can be useful in interpreting data obtained by on-line monitors.

Combinations of several types of probes can improve the information concerning corrosion of the system. Using only probes that provide corrosion-rate data cannot lead to as complete an analysis of the process and its effect on the equipment as with monitoring probes, which provide additional information.

Other Useful Information Obtained by Probes Both EIS and electrochemical noise probes can be used to determine information about the reactions that affect corrosion. Equivalent circuit analysis, when properly applied by an experienced engineer, can often give insight into the specifics of the corrosion reactions. Information such as corrosion product layer buildup, or inhibitor effectiveness, or coating breakdown can be obtained directly from analysis of the data from EIS or indirectly from electrochemical noise data. In most cases, this is merely making use of methodology developed in the corrosion laboratory.

Some assumptions must be made to do this, but these assumptions are no different from those made in the laboratory. Recent experience involving in-plant usage of EIS has shown that this technique can be used effectively as a monitoring method and has lead to development of several commercial systems.

Making use of the information from monitoring probes, combined with the storage and analysis capabilities of portable computers and microprocessors, seems the best method for understanding corrosion processes. Commercial setups can be assembled from standard probes, cables, readout devices, and storage systems. When these are coupled with analysis by corrosion engineers, the system can lead to better a understanding of in-plant corrosion processes.

Limitations of Probes and Monitoring Systems There are limitations even with the most up-to-date systems. Some of the things which cannot be determined using corrosion probes include:

Specifics on the type of biological attack. This must be done by some other method such as chemical analysis of the solution (plus consideration given to limitations to the use of these several electrochemical techniques for MIC studies, noted previously under "Corrosion Testing: Laboratory Tests" and subsequent subsections).

Actual lifetime of the plant equipment. Corrosion monitoring provides data, which must then be analyzed with additional input and interpretation. However, only estimates can be made of the lifetime of the equipment of concern. Lifetime predictions are, at best, carefully crafted guesses based on the best available data.

Choices of alternative materials. Corrosion probes are carefully chosen to be as close as possible to the alloy composition, heat treatment, and stress condition of the material that is being monitored. Care must be taken to ensure that the environment at the probe matches the service environment. Choices of other alloys or heat treatments and other conditions must be made by comparison. Laboratory testing or coupon testing in the process stream can be used to examine alternatives to the current material, but the probes and the monitors can only provide information about the conditions which are present during the test exposure and cannot extrapolate beyond those conditions.

Failure analysis. Often, for a corrosion-related failure, data from the probes are examined to look for telltale signs that could have led to detection of the failure. In some cases, evidence can be found that process changes were occurring which led to the failure. This does not mean that the probes should have detected the failure itself. Determination of an imminent corrosion-related failure is not possible, even with the most advanced monitoring system.

The aforementioned limitations are not problems with the probes or the monitoring systems but occur when information is desired that cannot be measured directly or which requires extrapolation. Many of the problems that are encountered with corrosion-monitoring systems and probes are related to the use to which probes are put.

Potential Problems with Probe Usage Understanding the electrochemical principles upon which probes are based helps to eliminate some of the potential problems with probes. However, in some situations, the information desired is not readily available.

For example, consider localized corrosion. Although data from corrosion probes indicate corrosion rate, it is not possible to tell that localized corrosion is the problem.

This is an example of measuring the wrong thing. In this case, the probes work adequately, the monitoring system is adequate, as is the monitoring interval, but detection of the type of corrosion cannot be made based on the available data. Different types of probes and testing are required to detect the corrosion problem.

Another problem can occur if the probes and monitors are working properly but the probe is placed improperly. Then the probe does not measure the needed conditions and environment. The data obtained by the probe will not tell the whole story.

An example of this is in a condenser where the corrosion probe is in a region where the temperature is lower than that at the critical condition of interest. Local scale buildup is another example of this type of situation, as is formation of a crevice at a specific location.

The type of probe, its materials, and method of construction must be carefully considered in designing an effective corrosion-monitoring system. Since different types of probes provide different types of information, it may be necessary to use several types.

Incorrect information can result if the probe is made of the wrong material and is not heat treated in the same way as the process equipment (as well as because of other problems). The probe must be as close as possible to the material from which the equipment of interest is made. Existence of a critical condition, such as weldments or galvanic couples or occluded cells in the equipment of concern, makes the fabrication, placement, and maintenance of the probes and monitoring system of critical importance, if accurate and useful data are to be obtained.

Before electrochemical techniques are used in the evaluation of any given, *viable* MIC environment/metal system, such a test protocol should receive considerable review by personnel quite experienced in *both* electrochemical testing and microbiologically influenced corrosion.

The data obtained from probes and monitoring systems are most useful when analyzed by a corrosion specialist. Data not taken, analyses not made, or expertise not sought can quickly lead to problems even with the most up-to-date corrosion probes and monitoring system.

ECONOMICS IN MATERIALS SELECTION

In most instances, there will be more than one alternative material which may be considered for a specific application. Calculation of true long-term costs requires estimation of the following:

1. Total cost of fabricated equipment and piping
2. Total installation cost
3. Service life
4. Maintenance costs: amount and timing
5. Time and cost requirements to replace or repair at the end of service life
6. Cost of downtime to replace or repair
7. Cost of inhibitors, extra control facilities, and so on, required to assure achievement of predicted service life
8. Time value of money
9. Factors which impact taxation, such as depreciation and tax rates
10. Inflation rate

Proper economic analysis will allow comparison of alternatives on a sound basis. Detailed calculations are beyond the scope of this section. The reader should review the material in the NACE Publication 3C194, Item No. 24182, "Economics of Corrosion," Sept., 1994.

PROPERTIES OF MATERIALS

GUIDE TO TABULATED DATA

Note from the Sec. 28 editors to the readers of this handbook: Historically, previous editions of *Perry's Chemical Engineers' Handbook* carried an extensive series of so-called corrosion resistance tables [listing recommended materials of construction (MOC) versus various corrosive environments]. This practice goes back, at least, to the Materials of Construction Sec. 18, 1941, 2d ed. Unfortunately, if valid at all, *these data are only usable as indicators of what will* **not** *work; for sure, these listings should* **not** *be used as recommendations of what materials are corrosion resistant.* The section editors have elected to no longer include these data tabulations.

Beyond the simple resistance of a material of construction to dissolution in a given chemical, many other properties enter into consideration when making an appropriate or optimum MOC selection for a given environmental exposure. These factors include the influence of velocity, impurities or contaminants, pH, stress, crevices, bimetallic couples, levels of nuclear, UV, or IR radiation, microorganisms, temperature heat flux, stray currents, properties associated with original production of the material and its subsequent fabrication as an item of equipment, as well as other physical and mechanical properties of the MOC, the *Proverbial Siebert Changes in the Phase of the Moon,* and so forth.

Therefore, the seventh edition no longer includes these endless tabulations of data; rather, there is an extensive coverage of corrosion mechanisms, the manner in which these various factors effect the corrosion system, as well as more detail as to the testing protocol necessary to assist in a sound MOC selection.

A few collections of more generic information as to the overall acid and alkali resistance of broad classes of materials remain. These are only intended to be used as *indicators* of the tendencies of these MOC to react; they are not included as a substitute for the application of good, sound engineering evaluations.

MATERIALS STANDARDS AND SPECIFICATIONS

There are obvious benefits to be derived from consensus standards which define the chemistry and properties of specific materials. Such standards allow designers and users of materials to work with confidence that the materials supplied will have the expected minimum properties. Designers and users can also be confident that comparable materials can be purchased from several suppliers. Producers are confident that materials produced to an accepted standard will find a ready market and therefore can be produced efficiently in large factories.

While a detailed treatment is beyond the scope of this section, a few of the organizations which generate standards of major importance to the chemical-process industries in the United States are listed here. An excellent overview is presented in the *Encyclopedia of Chemical Technology* (3d ed., Wiley, New York, 1978–1980).

1. **American National Standards Institute** (**ANSI**), formerly American Standards Association (ASA). ANSI promulgates the piping codes used in the chemical-process industries.
2. **American Society of Mechanical Engineers** (**ASME**). This society generates the Boiler and Pressure Vessel Codes.
3. **American Society for Testing and Materials** (**ASTM**). This society generates specifications for most of the materials used in the ANSI Piping Codes and the ASME Boiler and Pressure Vessel Codes.
4. **International Organization for Standardization** (**ISO**). This organization is engaged in generating standards for worldwide use. It has 80 member nations.

FERROUS METALS AND ALLOYS

Steel Carbon steel is the most common, cheapest, and most versatile metal used in industry. It has excellent ductility, permitting many cold-forming operations. Steel is also very weldable.

The grades of steel most commonly used in the chemical-process industries have tensile strength in the 345- to 485-MPa (50,000 to 70,000-lbf/in^2) range, with good ductility. Higher strength levels are achieved by cold work, alloying, and heat treatment.

Carbon steel is easily the most commonly used material in process plants despite its somewhat limited corrosion resistance. It is routinely used for most organic chemicals and neutral or basic aqueous solutions at moderate temperatures. It is also used routinely for the storage of concentrated sulfuric acid and caustic soda [up to 50 percent and 55°C (130°F)]. Because of its availability, low cost, and ease of fabrication steel is frequently used in services with corrosion rates of 0.13 to 0.5 mm/y (5 to 20 mils/y), with added thickness (**corrosion allowance**) to assure the achievement of desired service life. Product quality requirements must be considered in such cases.

Low-Alloy Steels Alloy steels contain one or more alloying agents to improve mechanical and corrosion-resistant properties over those of carbon steel.

A typical low-alloy grade [American Iron and Steel Institute (AISI) 4340] contains 0.40 percent C, 0.70 percent Mn, 1.85 percent Ni, 0.80 percent Cr, and 0.25 percent Mo. Many other alloying agents are used to produce a large number of standard AISI and proprietary grades.

Nickel increases toughness and improves low-temperature properties and corrosion resistance. Chromium and silicon improve hardness, abrasion resistance, corrosion resistance, and resistance to oxidation. Molybdenum provides strength at elevated temperatures.

The addition of small amounts of alloying materials greatly improves corrosion resistance to atmospheric environments but does not have much effect against liquid corrosives. The alloying elements produce a tight, dense adherent rust film, but in acid or alkaline solutions corrosion is about equivalent to that of carbon steel. However, the greater strength permits thinner walls in process equipment made from low-alloy steel.

Cast Irons Generally, cast iron is not a particularly strong or tough structural material, although it is one of the most economical and is widely used industrially.

Gray cast iron, low in cost and easy to cast into intricate shapes, contains carbon, silicon, managanese, and iron. Carbon (1.7 to 4.5 percent) is present as combined carbon and graphite; combined carbon is dispersed in the matrix as iron carbide (cementite), while free graphite occurs as thin flakes dispersed throughout the body of the metal. Various strengths of gray iron are produced by varying size, amount, and distribution of graphite.

Gray iron has outstanding damping properties—that is, ability to absorb vibration—as well as wear resistance. However, gray iron is brittle, with poor resistance to impact and shock. Machinability is excellent.

With some important exceptions, gray-iron castings generally have corrosion resistance similar to that of carbon steel. They do resist atmospheric corrosion as well as attack by natural or neutral waters and neutral soils. However, dilute acids and acid-salt solutions will attack this material.

Gray iron is resistant to concentrated acids (nitric, sulfuric, phosphoric) as well as to some alkaline and caustic solutions. Caustic fusion pots are usually made from gray cast iron with low silicon content; cast-iron valves, pumps, and piping are common in sulfuric acid plants.

White cast iron is brittle and difficult to machine. It is made by controlling the composition and rate of solidification of the molten iron so that all the carbon is present in the combined form. Very abrasive- and wear-resistant, white cast iron is used as liners and for grinding balls, dies, and pump impellers.

Malleable iron is made from white cast iron. It is cast iron with free carbon as dispersed nodules. This arrangement produces a tough, relatively ductile material. Total carbon is about 2.5 percent. Two types are produced: standard and pearlitic (combined carbon plus nodules). Standard malleable iron is easily machined; pearlitic, less so. Both types will withstand bending and cold working without cracking. Large welded areas are not recommended with fusion welding because welds are brittle. Corrosion resistance is about the same as for gray cast iron.

Ductile cast iron includes a group of materials with good strength, toughness, wear resistance, and machinability. This type of cast iron contains combined carbon and dispersed nodules of carbon. Composition is about the same as gray iron, with more carbon (3.7 percent) than malleable iron. The spheroidal graphite reduces the notch effect produced by graphite flakes, making the material more ductile.

There are a number of grades of ductile iron; some have maximum toughness and machinability; others have maximum resistance to oxidation.

Generally, corrosion resistance is similar to gray iron. But ductile iron can be used at higher temperatures—up to 590°C (1,100°F) and sometimes even higher.

Alloy Cast Irons Cast iron is not usually considered corrosion-resistant, but this condition can be improved by the use of various cast-iron alloys. A number of such materials are commercially available.

High-silicon cast irons have excellent corrosion resistance. Silicon content is 13 to 16 percent. This material is known as Durion. Adding 4 percent Cr yields a product called Durichlor, which has improved resistance in the presence of oxidizing agents. These alloys are not readily machined or welded.

Silicon irons are very resistant to oxidizing and reducing environments, and resistance depends on the formation of a passive film. These irons are widely used in sulfuric acid service, since they are unaffected by sulfuric at all strengths, even up to the boiling point.

Because they are very hard, silicon irons are good for combined corrosion-erosion service.

Another group of cast-iron alloys are called **Ni-Resist.** These materials are related to gray cast iron in that they have high carbon contents (3 percent), with fine graphite flakes distributed throughout the structure. Nickel contents range from 13.5 to 36 percent, and some have 6.5 percent Cu.

Generally, nickel-alloy castings have superior toughness and impact resistance compared with gray irons. The nickel-alloy castings can be welded and machined.

Corrosion resistance of nickel alloys is superior to that of cast irons but less than that of pure nickel. There is little attack from neutral or alkaline solutions. Oxidizing acids such as nitric are highly detrimental. Cold, concentrated sulfuric acid can be handled.

Ni-Resist has excellent heat resistance, with some grades serviceable up to 800°C (1,500°F). Also, a ductile variety is available, as well as a hard variety (Ni-Hard).

Stainless Steel There are more than 70 standard types of stainless steel and many special alloys. These steels are produced in the wrought form (AISI types) and as cast alloys [Alloy Casting Institute (ACI) types]. Generally, all are iron-based, with 12 to 30 percent chromium, 0 to 22 percent nickel, and minor amounts of carbon, niobium (columbium), copper, molybdenum, selenium, tantalum, and titanium. These alloys are very popular in the process industries. They are heat- and corrosion-resistant, noncontaminating, and easily fabricated into complex shapes.

There are three groups of stainless alloys: (1) martensitic, (2) ferritic, and (3) austenitic.

The **martensitic alloys** contain 12 to 20 percent chromium with controlled amounts of carbon and other additives. Type 410 is a typical member of this group. These alloys can be hardened by heat treatment, which can increase tensile strength from 550 to 1,380 MPa (80,000 to 200,000 lbf/in^2).

Corrosion resistance is inferior to that of austenitic stainless steels, and martensitic steels are generally used in mildly corrosive environments (atmospheric, fresh water, and organic exposures).

Ferritic stainless contains 15 to 30 percent Cr, with low carbon content (0.1 percent). The higher chromium content improves its corrosive resistance. Type 430 is a typical example. The strength of ferritic stainless can be increased by cold working but not by heat treatment. Fairly ductile ferritic grades can be fabricated by all standard methods. They are fairly easy to machine. Welding is not a problem, although it requires skilled operators.

Corrosion resistance is rated good, although ferritic alloys are not good against reducing acids such as HCl. But mildly corrosive solutions and oxidizing media are handled without harm. Type 430 is widely used in nitric acid plants. In addition, it is very resistant to scaling and high-temperature oxidation up to 800°C (1,500°F).

TABLE 28-2 General Corrosion Properties of Some Metals and Alloys*

Ratings:
0: Unsuitable. Not available in form required or not suitable for fabrication requirements or not suitable for corrosion conditions.
1: Poor to fair.
2: Fair. For mild conditions or when periodic replacement is possible. Restricted use.
3: Fair to good.
4: Good. Suitable when superior alternatives are uneconomic.
5: Good to excellent.
6: Normally excellent.
Small variations in service conditions may appreciably affect corrosion resistance. Choice of materials is therefore guided wherever possible by a combination of experience and laboratory and site tests.

	Nonoxidizing or reducing media				Liquids							Gases				
			Alkaline solutions, e.g.		Oxidizing media			Natural waters				Common industrial media				
								Freshwater supplies		Seawater		Steam		Furnace gases with incidental sulfur content		
Materials	Acid solutions, excluding hydrochloric e.g., phosphoric, sulfuric, most conditions, many organics	Neutral solutions, e.g., many nonoxidizing salt solutions, chlorides, sulfates	Caustic and mild alkalies, excluding ammonium hydroxide	Ammonium hydroxide and amines	Acid solutions, e.g., nitric	Neutral or alkaline solutions, e.g., per-sulfates, peroxides, chromates	Pitting media,† acid ferric chloride solutions	Static or slow-moving	Turbulent	Static or slow-moving	Turbulent	Moist, con-densate	Dry at high temperature, promoting slight dissociation	Reducing e.g., heat-treatment furnace gases	Oxidizing, e.g., flue gases	Ambient air, city or industrial
Cast iron, flake graphite, plain or low-alloy	1	3	4	5	0	4	0	4	3	4	2	4	4	1	1	3
Ductile iron (higher strength and hardness may be attained by composition and heat treatment or both)	1	3	4	5	0	4	0	4	4	4	3	4	4	1	1	3
Ni-Resist corrosion-resistant cast irons	4	5	5	5	0	5	0	5	5	5	5	5	5	3	2	4
14% silicon iron	6	6	2	5	6	6	3	5	5	5	5	6	4	4	3	6
Mild steel, also low-alloy irons and steels	1	3	4	5	0	4	0	4	3	4	2	4	4	1	1	3
Stainless steel, ferritic 17% Cr type	2	4	4	6	5	6	0	4	6	1	4	5	6	3	2	4
Stainless steel, austenitic 18 Cr; 8 Ni type	3	4	5	6	6	6	0	6	6	2	5	6	6	2	3	5

Stainless steel, austenitic 18 Cr; 12 Ni; 2.5 Mo type	4	5	5	6	5	6	1	6	6	3	5	6	6	2	4	6
Stainless steel, austenitic 20 Cr; 29 Ni; 2.5 Mo; 3.5 Cu type	5	6	5	6	5	6	2	6	6	4	6	6	6	2	4	6
Incoloy 825 nickel-iron-chromium alloy (40 Ni; 21 Cr; 3 Mo; 1.5 Cu; balance Fe)	6	6	5	6	5	6	2	6	6	4	6	6	6	2	5	6
Hastelloy alloy C-276 (55 Ni; 17 Mo; 16 Cr; 6 Fe; 4 W)	5	6	5	6	4	6	5	6	6	6	6	6	6	3	4	6
Hastelloy alloy B-2 (61 Ni; 28 Mo; 6 Fe)	6	5	4	4	0	3	0	6	6	4	4	6	5	3	2	5
Inconel 600 (78 Ni; 15 Cr; 7 Fe)	3	6	6	6	3	6	1	6	6	4	6	6	6	2	4	6
Copper-nickel alloys up to 30% nickel	4	5	5	0	0	4	1	6	6	6	6	6	5	2	2	5
Monel 400 nickel-copper alloy (66 Ni; 30 Cu; 2 Fe)	5	6	6	1	0	5	1	6	6	4	6	6	6	2	3	5
Nickel 200—commercial (99.4 Ni)	4	5	6	1	0	5	0	6	6	3	5	6	6	2	2	4
Copper and silicon bronze	4	4	4	0	0	4	0	6	5	4	1	6	5	2	2	5
Aluminum brass (76 Cu; 22 Zn; 2 Al)	3	4	2	0	0	3	0	6	6	4	5	6	5	2	2	5
Nickel-aluminum bronze (80 Cu; 10 Al; 5 Ni; 5 Fe)	4	4	2	0	0	3	0	6	6	4	5	6	5	2	3	5
Bronze, type A (88 Cu; 5 Sn; 5 Ni; 2 Zn)	4	5	4	0	0	4	0	6	6	5	5	6	5	2	2	5
Aluminum and its alloys	1	3	0	6	0–5	0–4	0	4	5	0–5	4	5	2	5	4	5
Lead, chemical or antimonial	5	5	2	2	0	2	0	6	5	5	3	2	0	4	3	5
Silver	4	6	6	0	0	2	0	6	6	5	5	6	5	4	4	4
Titanium	3	6	2	6	6	6	6	6	6	6	6	6	5	3	5	6
Zirconium	3	6	2	6	6	6	2	6	6	6	6	6	6	3	5	6

TABLE 28-2 General Corrosion Properties of Some Metals and Alloys* (*Concluded*)

Ratings:
0: Unsuitable. Not available in form required or not suitable for fabrication requirements or not suitable for corrosion conditions.
1: Poor to fair.
2: Fair. For mild conditions or when periodic replacement is possible. Restricted use.
3: Fair to good.
4: Good. Suitable when superior alternatives are uneconomic.
5: Good to excellent.
6: Normally excellent.
Small variations in service conditions may appreciably affect corrosion resistance. Choice of materials is therefore guided wherever possible by a combination of experience and laboratory and site tests.

Material	Gases (*continued*)				Available forms	Cold formability in wrought and clad form	Weldability	Maximum strength annealed condition × 1000 lb/in²	Coefficient of thermal expansion, millionths per °F, 70–212°F	Remarks¶
	Halogens and derivatives									
	Halogens		Halide acids, moist, e.g., hydrochloric hydrolysis products of organic halides	Hydrogen halides, dry,‡ e.g., dry hydrogen chloride, °F						
	Moist, e.g., chlorine below dew point	Dry, e.g., fluorine above dew point								
Cast iron, flake graphite, plain or low alloy	0	2	0	2 < 400 1 < 750	Cast	No	Fair§	45	6.7	
Ductile iron (higher strength and hardness may be attained by composition and heat treatment or both)	0	2	0	2 < 400 1 < 750	Cast	No	Good§	67	7.5	
Ni-Resist corrosion-resistant cast irons	0	2	3	3 < 400 2 < 750	Cast	No	Good§	22–31	10.3	
Durion—14% silicon iron	0	0	4	1 < 400	Cast	No	No	22	7.4	Very brittle, susceptible to cracking by mechanical and thermal shock
Mild steel, also low-alloy irons and steels	0	3	0	3 < 400 1 < 750	Wrought, cast	Good	Good	67	6.7	High strengths obtainable by alloying, also improved atmospheric corrosion resistance. See ASTM specifications for particular grade
Stainless steel, ferritic 17% Cr type	0	2	0	2 < 400	Wrought, cast, clad	Good	Good§	78	6.0	AISI type 430 ASTM corrosion- and heat-resisting steels
Stainless steel, austenitic 18 Cr; 8 Ni types	0	2	0	3 < 400	Wrought, cast, clad	Good	Good	90	9.6	AISI type 304 ASTM corrosion- and heat-resisting steels; stabilized or LC types used for welding
Stainless steel, austenitic 18 Cr; 12 Ni; 2.5 Mo type	0	3	2	4 < 400 3 < 750	Wrought, cast, clad	Good	Good	90	8.9	AISI type 316 ASTM corrosion- and heat-resisting steel; LC type used for welding

Stainless steel, austenitic 20 Cr; 29 Ni; 2.5 Mo; 3.5 Cu type	1	3	3	4 < 400 3 < 750	Wrought, cast	Good	Good	90	9.4	ACI CH-7M; good resistance to sulfuric, phosphoric, and fatty acids at elevated temperatures
Incoloy 825 nickel-iron-chromium alloy (40 Ni; 21 Cr; 3 Mo; 1.5 Cu; bal. Fe)	2	3	3	4 < 400 3 < 750	Wrought, cast, clad	Good	Good	100	7.3	Special alloy with good resistance to sulfuric, phosphoric, and fatty acids; resistant to chlorides in some environments
Hastelloy alloy C-276 (55 Ni; 17 Mo; 16 Cr; 6 Fe; 4 W)	5	4	4	4 < 750 3 < 900	Wrought, cast, clad	Fair	Good	145	6.3	Excellent resistance to wet chlorine gas and sodium hypochlorite solutions
Hastelloy alloy B-2 (61 Ni; 28 Mo; 6 Fe)	1	3	5	4 < 750 3 < 900	Wrought, cast, clad	Fair	Good	135	5.6	Resistant to solutions of hydrochloric and sulfuric acids
Inconel 600 (78 Ni; 15 Cr; 7 Fe)	2	5	3	5 < 400 4 < 900	Wrought, cast, clad	Good	Good	90	8.9	Wide application in food and pharmaceutical industries
Copper-nickel alloys up to 30% nickel	1	5	2	4 < 400 3 < 750	Wrought, cast, clad	Good	Good	38–62	9.3–8.5	High-iron types excellent for resisting high-velocity effects in condenser tubes
Monel 400 nickel-copper alloy (66 Ni; 30 Cu; 2 Fe)	2	6	3	6 < 400 3 < 750 2 < 900	Wrought, cast, clad	Good	Good	77	7.5	Widely used for sulfuric acid pickling equipment; also for propeller shafts in motor boats; precautions needed to avoid sulfur attack during fabrication
Nickel 200—commercial (99.4 Ni)	2	6	2	6 < 400 5 < 750 4 < 900	Wrought, cast, clad	Good	Good	54	6.6	Widely used for hot concentrated caustic solutions; precautions needed to avoid sulfur attack during fabrication
Copper and silicon bronze	0	5	2	3 < 400 2 < 750	Wrought, cast, clad	Excellent	Fair	29	9.3–9.5	Unsuitable for hot concentrated mineral acids or for high-velocity HF
Aluminum brass (76 Cu; 22 Zn; 2 Al)	0	4	2	2 < 400	Wrought, cast	Good	Fair	60	10.3	Possibility of developing localized corrosion in seawater
Nickel-aluminum bronze (80 Cu; 10 Al; 5 Ni; 5 Fe)	0	4	3	3 < 400 2 < 750	Wrought, cast	Good	Fair	60–80	9.4	Ship propellers an excellent application
Bronze, type A (88 Cu; 5 Sn; 5 Ni; 2 Zn)	0	4	3	3 < 400 2 < 750	Cast	No	§	45	11.0	High strengths obtained by heat treatment; not susceptible to dezincification
Aluminum and its alloys	0	6	0	3 < 400 1 < 750	Wrought, cast, clad	Good	Good	9–90	11.5–13.7	Extent of corrosion dependent upon type and concentration of acidic ions; wide range of mechanical properties obtainable by alloying and heat treatment
Lead, chemical or antimonial	0	1	3	0	Wrought, cast, clad	Excellent	Good	2	16.4–15.1	High purity "chemical lead" preferred for most applications
Silver	5	5	3	4 < 400 2 < 750	Wrought, cast, clad	Excellent	Good	21	10.6	Used as a lining
Titanium	6	0	1	0	Wrought, cast	Fair	Good§	6–90	5.0	Possibility of red fuming HNO_3 initiating explosions; good resistance to solutions containing chlorides
Zirconium	6	1	6	0	Wrought, cast	Fair	Good§			

*Data courtesy of International Nickel Co.
†On unsuitable materials these media may promote potentially dangerous pitting.
‡Temperatures are approximate.
§Special precautions required.
¶Many of these materials are suitable for resisting dry corrosion at elevated temperatures.

TABLE 28-3 Unified Alloy Numbering System (UNS)

UNS was established in 1974 by ASTM and SAE to reduce the confusion involved in the labeling of commercial alloys. Metals have been placed into 15 groups, each of which is given a code letter. The specific alloy is identified by a five-digit number following this code letter.

Nonferrous metals and alloys	
A00001–A99999	Aluminum and aluminum alloys
C00001–C99999	Copper and copper alloys
E00001–E99999	Rare-earth and rare-earth-like metals and alloys
L00001–L99999	Low-melting metals and alloys
M00001–M99999	Miscellaneous nonferrous metals and alloys
N00001–N99999	Nickel and nickel alloys
P00001–P99999	Precious metals and alloys
R00001–R99999	Reactive and refractory metals and alloys
Ferrous metals and alloys	
D00001–D99999	Specified-mechanical-properties steels
F00001–F99999	Cast irons and cast steels
G00001–G99999	AISI and SAE carbon and alloy steels
H00001–H99999	AISI H steels
K00001–K99999	Miscellaneous steels and ferrous alloys
S00001–S99999	Heat- and corrosion-resistant (stainless) steels
T00001–T99999	Tool steels

When possible, earlier widely used three- or four-digit alloy numbering systems such as those developed by the Aluminum Association (AA), Copper Development Association (CDA), American Iron and Steel Institute (AISI), etc., have been incorporated by the addition of the appropriate alloy-group code letter plus additional digits. For example:

Alloy description	Former designation		UNS designation
	System	No.	
Aluminum + 1.2% Mn	AA	3003	A93003
Copper, electrolytic tough pitch	CDA	110	C11000
Carbon steel, 0.2% C	AISI	1020	G10200
Stainless steel, 18 Cr, 8 Ni	AISI	304	S30400

Proprietary alloys are assigned numbers by the AA, AISI, CDA, ASTM, and SAE, which maintains master listings at their headquarters. Handbooks describing the system are available. (Cf. ASTM publication DS-56AC.)

SOURCE: ASTM DS-56A. *(Courtesy of National Association of Corrosion Engineers.)*

TABLE 28-4 Coefficient of Thermal Expansion of Common Alloys*

	UNS	10^{-6} in/(in·°F)	10^{-6} mm/(mm·°C)	Temperature range, °C
Aluminum alloy AA1100	A91100	13.1	24.	20–100
Aluminum alloy AA5052	A95052	13.2	24.	20–100
Aluminum cast alloy 43	A24430	12.3	22.	20–100
Copper	C11000	9.4	16.9	20–100
Red brass	C23000	10.4	18.7	20–300
Admiralty brass	C44300	11.2	20.	20–300
Muntz Metal	C28000	11.6	21.	20–300
Aluminum bronze D	C61400	9.0	16.2	20–300
Ounce metal	C83600	10.2	18.4	0–100
90-10 copper nickel	C70600	9.5	17.1	20–300
70-30 copper nickel	C71500	9.0	16.2	20–300
Carbon steel, AISI 1020	G10200	6.7	12.1	0–100
Gray cast iron	F10006	6.7	12.1	0–100
4-6 Cr, ½ Mo steel	S50100	7.3	13.1	20–540
Stainless steel, AISI 410	S41000	6.1	11.0	0–100
Stainless steel, AISI 446	S44600	5.8	10.4	0–100
Stainless steel, AISI 304	S30400	9.6	17.3	0–100
Stainless steel, AISI 310	S31000	8.0	14.4	0–100
Stainless steel, ACI HK	J94224	9.4	16.9	20–540
Nickel alloy 200	N02200	7.4	13.3	20–90
Nickel alloy 400	N04400	7.7	13.9	20–90
Nickel alloy 600	N06600	7.4	13.3	20–90
Nickel-molybdenum alloy B-2	N10665	5.6	10.1	20–90
Nickel-molybdenum alloy C-276	N10276	6.3	11.3	20–90
Titanium, commercially pure	R50250	4.8	8.6	0–100
Titanium alloy T1-6A1-4V	R56400	4.9	8.8	0–100
Magnesium alloy AZ31B	M11311	14.5	26.	20–100
Magnesium alloy AZ91C	M11914	14.5	26.	20–100
Chemical lead		16.4	30.	0–100
50-50 solder	L05500	13.1	24.	0–100
Zinc	Z13001	18.	32.	0–100
Tin	L13002	12.8	23.	0–100
Zirconium	R60702	2.9	5.2	0–100
Molybdenum	R03600	2.7	4.9	20–100
Tantalum	R05200	3.6	6.5	20–100

*Courtesy of National Association of Corrosion Engineers.

Austenitic stainless steels are the most corrosion-resistant of the three groups. These steels contain 16 to 26 percent chromium and 6 to 22 percent nickel. Carbon is kept low (0.08 percent maximum) to minimize carbide precipitation. These alloys can be work-hardened, but heat treatment will not cause hardening. Tensile strength in the annealed condition is about 585 MPa (85,000 lbf/in^2), but work-hardening can increase this to 2,000 MPa (300,000 lbf/in^2). Austenitic stainless steels are tough and ductile.

They can be fabricated by all standard methods. But austenitic grades are not easy to machine; they work-harden and gall. Rigid machines, heavy cuts, and high speeds are essential. Welding, however, is readily performed, although welding heat may cause chromium carbide precipitation, which depletes the alloy of some chromium and lowers its corrosion resistance in some specific environments, notably nitric acid. The carbide precipitation can be eliminated by heat treatment (solution annealing). To avoid precipitation, special stainless steels stabilized with titanium, niobium, or tantalum have been developed (types 321, 347, and 348). Another approach to the problem is the use of low-carbon steels such as types 304L and 316L, with 0.03 percent maximum carbon.

The addition of molybdenum to the austenitic alloy (types 316, 316L, 317, and 317L) provides generally better corrosion resistance and improved resistance to pitting.

In the stainless group, nickel greatly improves corrosion resistance over straight chromium stainless. Even so, the chromium-nickel steels, particularly the 18-8 alloys, perform best under **oxidizing conditions,** since resistance depends on an oxide film on the surface of the alloy. Reducing conditions and chloride ions destroy this film and bring on rapid attack. Chloride ions tend to cause pitting and crevice corrosion; when combined with high tensile stresses, they can cause stress-corrosion cracking.

Cast stainless alloys are widely used in pumps, valves, and fittings. These casting alloys are designated under the ACI system. All corrosion-resistant alloys have the letter C plus a second letter (A to N) denoting increasing nickel content. Numerals indicate maximum carbon. While a rough comparison can be made between ACI and AISI types, compositions are not identical and analyses cannot be used interchangeably. Foundry techniques require a rebalancing of the wrought chemical compositions. However, corrosion resistance is not greatly affected by these composition changes. Typical members of this group are CF-8, similar to type 304 stainless; CF-8M, similar to type 316; and CD-4M Cu, which has improved resistance to nitric, sulfuric, and phosphoric acids.

In addition to the C grades, there is a series of heat-resistant grades of ACI cast alloys, identified similarly to the corrosion-resistant grades, except that the first letter is H rather than C. Mention should

TABLE 28-5 Melting Temperatures of Common Alloys*

	UNS	Melting range °F	Melting range °C
Aluminum alloy AA1100	A91100	1190–1215	640–660
Aluminum alloy AA5052	A95052	1125–1200	610–650
Aluminum cast alloy 43	A24430	1065–1170	570–630
Copper	C11000	1980	1083
Red brass	C23000	1810–1880	990–1025
Admiralty brass	C44300	1650–1720	900–935
Muntz Metal	C28000	1650–1660	900–905
Aluminum bronze D	C61400	1910–1940	1045–1060
Ounce metal	C83600	1510–1840	854–1010
Manganese bronze	C86500	1583–1616	862–880
90-10 copper nickel	C70600	2010–2100	1100–1150
70-30 copper nickel	C71500	2140–2260	1170–1240
Carbon steel, AISI 1020	G10200	2760	1520
Gray cast iron	F10006	2100–2200	1150–1200
4-6 Cr, ½ Mo Street	S50100	2700–2800	1480–1540
Stainless steel, AISI 410	S41000	2700–2790	1480–1530
Stainless steel, AISI 446	S44600	2600–2750	1430–1510
Stainless steel, AISI 304	S30400	2550–2650	1400–1450
Stainless steel, AISI 310	S31000	2500–2650	1400–1450
Stainless steel, ACI HK	J94224	2550	1400
Nickel alloy 200	N02200	2615–2635	1440–1450
Nickel alloy 400	N04400	2370–2460	1300–1350
Nickel alloy 600	N06600	2470–2575	1350–1410
Nickel-molybdenum alloy B-2	N10665	2375–2495	1300–1370
Nickel-molybdenum alloy C-276	N10276	2420–2500	1320–1370
Titanium, commercially pure	R50250	3100	1705
Titanium alloy T1-6A1-4V	R56400	2920–3020	1600–1660
Magnesium alloy AZ 31B	M11311	1120–1170	605–632
Magnesium alloy HK 31A	M13310	1092–1204	589–651
Chemical lead		618	326
50-50 solder	L05500	361–421	183–216
Zinc	Z13001	787	420
Tin	Z13002	450	232
Zirconium	R60702	3380	1860
Molybdenum	R03600	4730	2610
Tantalum	R05200	5425	2996

*Courtesy of National Association of Corrosion Engineers.

also be made of precipitation-hardening (PH) stainless steels, which can be hardened by heat treatments at moderate temperatures. Very strong and hard at high temperatures, these steels have but moderate corrosion resistance. A typical PH steel, containing 17 percent Cr, 7 percent Ni, and 1.1 percent Al, has high strength, good fatigue properties, and good resistance to wear and cavitation corrosion. A large number of these steels with varying compositions are commercially available. Essentially, they contain chromium and nickel with added alloying agents such as copper, aluminum, beryllium, molybdenum, nitrogen, and phosphorus.

Medium Alloys A group of (mostly) proprietary alloys with somewhat better corrosion resistance than stainless steels are called medium alloys. A popular member of this group is the **20 alloy,** made by a number of companies under various trade names. Durimet 20 is a well-known cast version, containing 0.07 percent C, 29 percent Ni, 20 percent Cr, 2 percent Mo, and 3 percent Cu. The ACI designation of this alloy is CN-7M. A wrought form is known as Carpenter 20 (Cb3). Worthite is another proprietary 20 alloy with about 24 percent Ni and 20 percent Cr. The 20 alloy was originally developed to fill the need for a material with sulfuric acid resistance superior to the stainless steels.

Other members of the medium-alloy group are **Incoloy 825** and **Hastelloy G-3 and G-30.** Wrought Incoloy 825 has 40 percent Ni, 21 percent Cr, 3 percent Mo, and 2.25 percent Cu. Hastelloy G-3 contains 44 percent Ni, 22 percent Cr, 6.5 percent Mo, and 0.05 percent C maximum.

These alloys have extensive applications in sulfuric acid systems. Because of their increased nickel and molybdenum contents they are more tolerant of chloride-ion contamination than standard stainless steels. The nickel content decreases the risk of stress-corrosion cracking; molybdenum improves resistance to crevice corrosion and pitting.

High Alloys The group of materials called high alloys all contain relatively large percentages of nickel. **Hastelloy B-2** contains 61 percent Ni and 28 percent Mo. It is available in wrought and cast forms. Work hardening presents some fabrication difficulties, and machining is somewhat more difficult than for type 316 stainless. Conventional welding methods can be used. The alloy has unusually high resistance to all concentrations of hydrochloric acid at all temperatures in the absence of oxidizing agents. Sulfuric acid attack is low for all concentrations at 65°C (150°F), but the rate goes up with temperature. Oxidizing acids and salts rapidly corrode Hastelloy B. But alkalies and alkaline solutions cause little damage.

Chlorimet 2 has 63 percent Ni and 32 percent Mo and is somewhat similar to Hastelloy B-2. It is available only in cast form, mainly as valves and pumps. This is a tough alloy, very resistant to mechanical and thermal shock. It can be machined with carbide-tipped tools and welded with metal-arc techniques.

Hastelloy C-276 is a nickel-based alloy containing chromium (15.5 percent), molybdenum (15.5 percent), and tungsten (3 percent) as major alloying elements. It is available only in wrought form. This alloy is a low-impurity modification of Hastelloy C, which is still available in cast form. The low impurity level substantially reduces the risk of intergranular corrosion of grain-boundary precipitation in weld-heat-affected zones. This alloy is resistant to strong oxidizing chloride solutions, such as wet chlorine and hypochlorite solutions. It is one of the very few alloys which are totally resistant to seawater.

Hastelloy C-4 is almost totally immune to selective intergranular corrosion in weld-heat-affected zones with high temperature stability in the 650–1040°C (1200–1900°F) range; Hastelloy C-22 has better overall corrosion resistance and versatility than either C-4 or C-276 (in most environments).

Chlorimet 3 is an alloy, available only in cast form, which is similar in alloy content and corrosion resistance to Hastelloy C.

Inconel 600 (80 percent Ni, 16 percent Cr, and 7 percent Fe) should also be mentioned as a high alloy. It contains no molybdenum. The corrosion-resistant grade is recommended for reducing-oxidizing environments, particularly at high temperatures. When heated in air, this alloy resists oxidation up to 1,100°C (2,000°F). The alloy is outstanding in resisting corrosion by gases when these gases are essentially sulfur-free.

The alloys discussed are typical examples of the large number of proprietary high alloys used in the chemical industry. For more comprehensive lists and data, refer to the listed references.

NONFERROUS METALS AND ALLOYS

Nickel and Nickel Alloys Nickel is available in practically any mill form as well as in castings. It can be machined easily and joined by welding. Generally, oxidizing conditions favor corrosion, while reducing conditions retard attack. Neutral alkaline solutions, seawater, and mild atmospheric conditions do not affect nickel. The metal is widely used for handling alkalies, particularly in concentrating, storing, and shipping high-purity caustic soda. Chlorinated solvents and phenol are often refined and stored in nickel to prevent product discoloration and contamination.

A large number of nickel-based alloys are commercially available. Many have been mentioned in the preceding discussion of alloy castings and high alloys. One of the best known of these is **Monel 400,** 67 percent Ni and 30 percent Cu. It is available in all standard forms. This nickel-copper alloy is ductile and tough and can be readily fabricated and joined. Its **corrosion resistance** is generally superior to that of its components, being more resistant than nickel in reducing environments and more resistant than copper in oxidizing environments. The alloy can be used for relatively dilute sulfuric acid (below 80 percent), although aeration will result in increased corrosion. Monel will handle hydrofluoric acid up to 92 percent and 115°C

TABLE 28-6 Carbon and Low-Alloy Steels[a]

Steel type	ASTM	UNS	Composition, %[b]	Mechanical properties[c]		
				Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation, %
C-Mn	A53B	K03005	0.30 C, 1.20 Mn	35 (241)	60 (415)	
C-Mn	A106B	K03006	0.30 C, 0.29–1.06 Mn, 0.10 min. Si	35 (241)	60 (415)	30
C	A285A	K01700	0.17 C, 0.90 Mn	24 (165)	45–55 (310–380)	30
HSLA	A517F	K11576	0.08–0.22 C, 0.55–1.05 Mn, 0.13–0.37 Si, 0.36–0.79 Cr, 0.67–1.03 Ni, 0.36–0.64 Mo, 0.002–0.006 B, 0.12–0.53 Cu, 0.02–0.09 V	100 (689)	115–135 (795–930)	16
HSLA	A242(1)	K11510	0.15 C, 1.00 Mn, 0.20 min Cu, 0.15 P	42–50 (290–345)	63–70 (435–480)	21
2¼ Cr, 1 Mo	A387(22)	K21590	0.15 C, 0.30–0.60 Mn, 0.5 Si, 2.00–2.50 Cr, 0.90–1.10 Mo	30 (205)[d] 45 (310)[e]	60–85 (415–585)[d] 75–100 (515–690)[e]	18[c] 18[d]
4–6 Cr, ½ Mo	A335 (P5)	K41545	0.15 C, 0.30–0.60 Mn, 0.5 Si, 4.00–6.00 Cr, 0.45–0.65 Mo	30 (205)	60 (415)	
9 Cr, 1 Mo	A335 (P9)	K81590	0.15 C, 0.30–0.6 Mn, 0.25–1.00 Si, 8.00–10.00 Cr, 0.90–1.10 Mo	30 (205)	60 (415)	
9 Ni	A333(8), A353(1)	K81340	0.13 C, 0.90 Mn, 0.13–0.32 Si, 8.40–9.60 Ni	75 (515)	100–120 (690–825)	20
	AISI 4130	G41300	0.28–0.33 C, 0.80–1.10 Mn, 0.15–0.3 Si, 0.8–1.10 Cr, 0.15–0.25 Mo	120 (830)[f]	140 (965)[f]	22[f]
	AISI 4340	G43400	0.38–0.43 C, 0.60–0.80 Mn, 0.15–0.3 Si, 0.70–0.90 Cr, 1.65–2.00 Ni, 0.20–0.30 Mo	125 (860)[g]	148 (1020)[g]	20[g]

[a]Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
[b]Single values are maximum values unless otherwise noted.
[c]Room-temperature properties. Single values are minimum values.
[d]Class 1.
[e]Class 2.
[f]1-in-diameter bars water-quenched from 1,575°F (860°C) and tempered at 1,200°F (650°C).
[g]1-in-diameter bars oil-quenched from 1,550°F (845°C) and tempered at 1,200°F (650°C).

(235°F). Alkalies have little effect on this alloy, but it will not stand up against very highly oxidizing or reducing environments.

Aluminum and Alloys Aluminum and its alloys are made in practically all the forms in which metals are produced, including castings. Thermal conductivity of aluminum is 60 percent of that of pure copper, and unalloyed aluminum is used in many heat-transfer applications. Its high electrical conductivity makes aluminum popular in electrical applications. Aluminum is one of the most workable of metals, and it is usually joined by inert-gas-shielded arc-welding techniques.

Commercially pure aluminum has a tensile strength of 69 MPa (10,000 lbf/in²), but it can be strengthened by cold working. One limitation of aluminum is that strength declines greatly above 150°C (300°F). When strength is important, 200°C (400°F) is usually considered the highest permissible safe temperature for aluminum. However, aluminum has excellent low-temperature properties; it can be used at −250°C (−420°F).

Aluminum has high resistance to atmospheric conditions as well as to industrial fumes and vapors and fresh, brackish, or salt waters. Many mineral acids attack aluminum, although the metal can be used with concentrated nitric acid (above 82 percent) and glacial acetic acid. Aluminum cannot be used with strong caustic solutions.

It should be noted that a number of **aluminum alloys** are available (see Table 28-16). Many have improved mechanical properties over pure aluminum. The wrought heat-treatable aluminum alloys have tensile strengths of 90 to 228 MPa (13,000 to 33,000 lbf/in²) as annealed; when they are fully hardened, strengths can go as high as 572 MPa (83,000 lbf/in²). However, aluminum alloys usually have lower corrosion resistance than the pure metal. The **alclad** alloys have been developed to overcome this shortcoming. Alclad consists of an aluminum layer metallurgically bonded to a core alloy.

The corrosion resistance of aluminum and its alloys tends to be very sensitive to trace contamination. Very small amounts of metallic mercury, heavy-metal ions, or chloride ions can frequently cause rapid failure under conditions which otherwise would be fully acceptable.

When alloy steels do not give adequate corrosion protection—particularly from sulfidic attack—steel with an **aluminized surface coating** can be used. A spray coating of aluminum on a steel is not likely to spall or flake, but the coating is usually not continuous and may leave some areas of the steel unprotected. Hot-dipped "aluminized" steel gives a continuous coating and has proved satisfactory in a number of applications, particularly when sulfur or hydrogen sulfide is present. It is also used to protect thermal insulation and as weather shields for equipment. The coated steel resists fires better than solid aluminum.

Copper and Alloys Copper and its alloys are widely used in chemical processing, particularly when heat and electrical conductivity are important factors. The thermal conductivity of copper is twice that of aluminum and 90 percent that of silver. A large number of cop-

TABLE 28-7 Properties of Low-Alloy AISI Steels

AISI type	Typical physical properties[a]: Melting temperature, °F	Thermal conductivity, Btu/[(h·ft²)(°F/ft)] (212°F)	Coefficient of thermal expansion (0–1,200°F) per °F	Specific heat (68–212°F), Btu/(lb · °F)
13XX		27	7.9×10^{-6}[b]	0.10–0.11
23XX	2,600–2,620	38.3[c]	8.0×10^{-6}	0.11–0.12
25XX	2,610–2,620	34.5–38.5[c]	7.8×10^{-6}	0.11–0.12
40XX		27	8.3×10^{-6}[b]	0.10–0.11
41XX		24.7[d]		0.11
43XX	2,740–2,750	21.7[c]	8.1×10^{-6}	0.107
46XX		27[d]	6.3×10^{-6}[e]	0.10–0.11
48XX	2,750	26[f]	8.6×10^{-6}	
51XX	2,720–2,760	27–34[g]	7.4×10^{-6}[h]	0.10–0.11
61XX		27	8.1×10^{-6}[b]	0.10–0.11
86, 87XX	2,745–2,755	21.7[c]	8.2×10^{-6}	0.107
92, 94XX		27	8.1×10^{-6}[b]	0.10–0.12

XX = nominal percent carbon.
[a]Density for all low-alloy steels is about 0.28 lb/in³.
[b]68 to 1200°F.
[c]120°F.
[d]68°F.
[e]0 to 200°F.
[f]75°F.
[g]32 to 212°F.
[h]100 to 518°F.

TABLE 28-7 Properties of Low-Alloy AISI Steels (*Concluded*)

	Typical mechanical properties[a]					
AISI type	Tensile strength, 1,000 lbf/in²	Yield strength (0.2% offset), 1000 lbf/in²	Elongation (in 2 in), %	Reduction of area, %	Hardness, Brinell	Impact strength (Izod), ft·lbf
1,330[b]	122	100	19	52	248	
1,335[c]	126	105	20	59	262	
1,340[c]	137	118	19	55	285	
2,317[c]	107	72	27	71	222	84
2,515[c]	113	94	25	69	233	85
E2,517[c]	120	100	22	66	244	80
4,023[d]	120	85	20	53	255	
4,032[e]	210	182	11	49	415	
4,042[f]	235	210	10	42	461	
4,053[g]	250	223	12	40	495	
4,063[h]	269	231	8	15	534	
4,130[i]	200	170	16	49	375	25
4,140[j]	200	170	15	48	385	16
4,150[k]	230	215	10	40	444	12
4,320[d]	180	154	15	50	360	32
4,337[k]	210	140	14	50	435	18
4,340[k]	220	200	12	48	445	16
4,615[d]	100	75	18	52		42
4,620[d]	130	95	21	65		68
4,640[f]	185	160	14	52	390	25
4,815[d]	150	125	18	58	325	44
4,817[d]			15	52	355	36
4,820[i]			13	47	380	28
5,120[d]	143	114	13	45	302	6
5,130[m]	189	175	13	51	380	
5,140[m]	190	170	13	43	375	16
5,150[m]	224	208	10	40	444	
6,120[n]	125	94	21	56		28
6,145[o]	176	169	16	52	429	20
6,150[o]	187	179	13	42	444	13
8,620[p]	122	98	21	63	245	76
8,630[p]	162	142	14	54	325	42
8,640[p]	208	183	13	43	420	18
8,650[p]	214	194	12	41	423	
8,720[p]	122	98	21	63	245	76
8,740[p]	208	183	13	43	420	18
8,750[p]	214	194	12	41	423	
9,255[p]	232[q]	215	9	21	477	6
9,261[p]	258[r]	226	10	30	514	12

[a]Properties are for materials hardened and tempered as follows: [b]water-quenched from 1,525°F, tempered at 1,000°F; [c]oil-quenched from 1,525°F, tempered at 1,000°F, [d]pseudocarburized 8 h at 1700°F, oil-quenched, tempered 1 h at 300°F, [e]water-quenched from 1,525°F, tempered at 600°F, [f]oil-quenched from 1,500°F, tempered at 600°F, [g]oil-quenched from 1,475°F, tempered at 600°F, [h]oil-quenched from 1,450°F, tempered at 600°F, [i]water-quenched from 1,500 to 1,600°F, tempered at 800°F, [j]oil-quenched from 1,550°F, tempered at 800°F, [k]oil-quenched from 1,525°F, tempered at 800°F, [l]normalized at 1,650°F, reheated to 1,475°F, oil-quenched, tempered at 800°F, [m]normalized at 1,625°F, reheated to 1,550°F, water-quenched, tempered at 800°F; [n]carburized 10 h at 1,680°F, pot-cooled, oil-quenched from 1,525°F, tempered at 300°F; [o]normalized at 1,600°F, oil-quenched from 1,575°F, tempered at 1,000°F, [p]oil-quenched tempered at 800°F; [q]normalized at 1,650°F, reheated to 1,625°F, quenched in agitated oil, tempered at 800°F, [r]normalized at 1,600°F, reheated to 1,575°F, quenched in agitated oil, tempered at 800°F.

NOTE: °C = (°F − 32) × 5/9. To convert Btu/(h · ft · °F) to W/(m · °C), multiply by 0.8606; to convert Btu/(lbf · °F) to kJ/(kg · °C), multiply by 0.2388; to convert lbf/in² to MPa, multiply by 0.006895; and to convert ft · lbf to J, multiply by 0.7375.

per alloys are available, including brasses (Cu-Zn), bronzes (Cu-Sn), and cupronickels.

Copper has excellent low-temperature properties and is used at –200°C (–320°F). Brazing and soldering are common joining methods for copper, although welding, while difficult, is possible. Generally, copper has high resistance to industrial and marine atmospheres, seawater, alkalies, and solvents. Oxidizing acids rapidly corrode copper. However, the alloys have somewhat different properties than commercial copper.

Brasses with up to 15 percent Zn are ductile but difficult to machine. Machinability improves with increasing zinc up to 36 percent Zn. Brasses with less than 20 percent Zn have corrosion resistance equivalent to that of copper but with better tensile strengths. Brasses with 20 to 40 percent Zn have lower corrosion resistance and are subject to dezincification and stress-corrosion cracking, especially when ammonia is present.

Bronzes are somewhat similar to brasses in mechanical properties and to high-zinc brasses in corrosion resistance (except that bronzes are not affected by stress cracking). **Aluminum and silicon bronzes** are very popular in the process industries because they combine good strength with corrosion resistance.

Cupronickels (10 to 30 percent Ni) have become very important as copper alloys. They have the highest corrosion resistance of all copper alloys and find application as heat-exchanger tubing. Resistance to seawater is particularly outstanding.

Lead and Alloys Chemical leads of 99.9+ percent purity are used primarily in the chemical industry in environments that form thin, insoluble, and self-repairable protective films, for example, salts such as sulfates, carbonates, or phosphates. More soluble films such as nitrates, acetates, or chlorides offer little protection.

Alloys of antimony, tin, and arsenic offer limited improvement in mechanical properties, but the usefulness of lead is limited primarily because of its poor structural qualities. It has a low melting point and a high coefficient of expansion, and it is a very ductile material that will creep under a tensile stress as low as 1 MPa (145 lbf/in²).

Titanium Titanium has become increasingly important as a construction material. It is strong and of medium weight. Corrosion resistance is very superior in oxidizing and mild reducing media (Ti-Pd alloys Grade 7 and 11 have superior resistance in reducing environments, as does the Ti-Mo-Ni alloy Grade 12). Titanium is usually not bothered by impingement attack, crevice corrosion, and pitting attack in seawater. Its general resistance to seawater is excellent. Titanium is resistant to nitric acid at all concentrations except with red fuming nitric. The metal also resists ferric chloride, cupric chloride, and other hot chloride solutions. However, there are a number of disadvantages to titanium which have limited its use. Titanium is not easy to form, it has a high springback and tends to gall, and welding must be carried out in an inert atmosphere.

Zirconium Zirconium was originally developed as a construction material for atomic reactors. Reactor-grade zirconium contains very little hafnium, which would alter zirconium's neutron-absorbing properties. Commercial-grade zirconium, for chemical process applications, however, contains 2.5 percent hafnium. Zirconium resembles titanium from a fabrication standpoint. All welding must be done under an inert atmosphere. Zirconium has excellent resistance to reducing environments. Oxidizing agents frequently cause accelerated attack. It resists all chlorides except ferric and cupric. Zirconium alloys should *not* be used in concentrations of sulfuric acid above about 70 percent. There are a number of alloys of titanium and zirconium, with mechanical properties superior to those of the pure metals. The zirconium alloys are referred to as Zircaloys.

Tantalum The physical properties of tantalum are similar to those of mild steel except that tantalum has a higher melting point. Tantalum is ductile and malleable and can be worked into intricate forms. It can be welded by using inert-gas-shielded techniques. The metal is practically inert to many oxidizing and reducing acids (except fuming sulfuric). It is attacked by hot alkalies and hydrofluoric acid. Its cost generally limits use to heating coils, bayonet heaters, coolers, and condensers operating under severe conditions. When economically justified, larger items of equipment (reactors, tanks, etc.) may be fabricated with tantalum liners, either loose (with proper anchoring) or explosion-bonded-clad. Since tantalum linings are usually very thin, very careful attention to design and fabrication details is required.

INORGANIC NONMETALLICS

Glass and Glassed Steel Glass is an inorganic product of fusion which is cooled to a rigid condition without crystallizing. With unique

TABLE 28-8 Cast-Iron Alloys*

Alloy	ASTM	UNS	Composition, %†	Condition	Mechanical properties‡			
					Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation, %	Hardness, HB
Gray cast iron	A159 (G3000)	F10006	3.1–3.4 C, 0.6–0.9 Mn, 1.9–2.3 Si	As cast		30 (207)		187–241
Malleable cast iron	A602 (M3210)	F20000	2.2–2.9 C, 0.15–1.25 Mn, 0.9–1.90 Si	Annealed	32 (229)	50 (345)	12	130
Ductile cast iron	A395 (60-40-18)	F32800	None specified	Annealed	40 (276)	60 (414)	18	170
Cast iron	A436(1)	F41000	3.0 C, 1.5–2.5 Cr, 5.5–7.5 Cu, 0.5–1.5 Mn, 13.5–17.5 Ni, 1.0–2.8 Si	As cast		25 (172)		150
Cast iron	A436(2)	F41002	3.0 C, 1.5–2.5 Cr, 0.50 Cu, 0.5–1.5 Mn, 18–22 Ni, 1.0–2.8 Si	As cast		25 (172)		145
Cast iron	A436(5)	F41006	2.4 C, 0.1 Cr, 0.5 Cu, 0.5–1.5 Mn, 34–36 Ni, 1.0–2.0 Si	As cast		20 (138)		110
Ductile austenitic cast iron	A439(D-2)	F43000	3.0 C, 1.75–2.75 Cr, 0.7–1.25 Mn, 18–22 Ni, 1.5–3.0 Si	As cast	30 (207)	58 (400)		170
Ductile austenitic cast iron	A439 (D-5)	F43006	2.4 C, 0.1 Cr, 1.0 Mn, 34–36 Ni, 1.0–2.8 Si	As cast	30 (207)	55 (379)		155
Silicon cast iron	A518	F47003	0.7–1.1 C, 0.5 Cr, 0.5 Cu, 1.50 Mn, 0.5 Mo, 14.2–14.75 Si	As cast		16 (110)		520

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
†Single values are maximum values.
‡Typical room-temperature properties.

properties compared with metals, they require special considerations in their design and use.

Glass has excellent resistance to all acids except hydrofluoric and hot, concentrated H_3PO_4. It is also subject to attack by hot alkaline solutions. Glass is particularly suitable for piping when transparency is desirable.

The chief drawback of glass is brittleness, and it is also subject to damage by thermal shock. However, glass armored with epoxy-polyester fiberglass can readily be protected against breakage. On the other hand, glassed steel combines the corrosion resistance of glass with the working strength of steel. Accordingly, **glass linings** are resistant to all concentrations of hydrochloric acid to 120°C (250°F), to dilute concentrations of sulfuric to the boiling point, to concentrated sulfuric to 230°C (450°F), and to all concentrations of nitric acid to the boiling point. Acid-resistant glass with improved alkali resistance (up to 12 pH) is available.

A nucleated crystalline ceramic-metal composite form of glass has superior mechanical properties compared with conventional glassed steel. Controlled high-temperature firings chemically and physically bond the ceramic to steel, nickel-based alloys, and refractory metals. These materials resist corrosive hydrogen chloride gas, chlorine, or sulfur dioxide at 650°C (1,200°F). They resist all acids except HF up to 180°C (350°F). Their impact strength is 18 times that of safety glass; abrasion resistance is superior to that of porcelain enamel. They have 3 to 4 times the thermal-shock resistance of glassed steel.

Porcelain and Stoneware Porcelain and stoneware materials are about as resistant to acids and chemicals as glass, but with the advantage of greater strength. This is offset somewhat by poor ther-

TABLE 28-9 Standard Wrought Martensitic Stainless Steels*

AISI type	UNS	Composition, %†					Mechanical properties‡			
		Cr	Ni	Mo	C	Other	Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation, %	Hardness, HB
403	S40300	11.5–13.0			0.15		40 (276)	75 (517)	35	155
410	S41000	11.5–13.5			0.15		35 (241)	70 (483)	30	150
414	S41400	11.5–13.5	1.25–2.5		0.15		90 (621)	115 (793)	20	235
416	S41600	12–14		0.6	0.15	0.15S§	40 (276)	75 (517)	30	155
416Se	S41623	12–14			0.15	0.15Se§	40 (276)	75 (517)	30	155
420	S42000	12–14			0.15		50 (345)	95 (655)	20	195
420F	S42020	12–14		0.6	0.15§	0.15S§	55 (379)	95 (655)	22	220
422	S42200	11–13	0.5–1.0	0.75–1.25	0.20–0.25	0.15–0.30 V, 0.75–1.25 W	125 (862)	145 (1000)	18	320
431	S43100	15–17	1.25–2.5		0.20		95 (665)	125 (862)	20	260
440A	S44002	16–18		0.75	0.6–0.75		60 (414)	105 (724)	20	210
440B	S44003	16–18.0		0.75	0.75–0.95		62 (427)	107 (738)	18	215
440C	S44004	16–18		0.75	0.95–1.20		65 (448)	110 (758)	14	220
501	S50100	4–6		0.40–0.65	0.10§		30 (207)	70 (483)	28	160
502	S50200	4–6		0.40–0.65	0.10		25 (172)	65 (448)	30	150

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
†Single values are maximum values unless otherwise noted.
‡Typical room-temperature properties of annealed plates.
§Minimum.

TABLE 28-10 Standard Wrought Ferritic Stainless Steels*

AISI type	Composition, %† UNS	Cr	C	Mn	Si	P	S	Other	Mechanical properties‡ Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation, %	Hardness, HB
405	S40500	11.5–14.5	0.08	1.0	1.0	0.04	0.03	0.1–0.3 Al	40 (276)	65 (448)	30	150
409	S40900	10.5–11.75	0.08	1.0	1.0	0.045	0.045	(6 × C) Ti§	35 (241)	65 (448)	25	137
429	S42900	14–16	0.12	1.0	1.0	0.04	0.03		40 (276)	70 (483)	30	163
430	S43000	16–18	0.12	1.0	1.0	0.04	0.03		40 (276)	75 (517)	30	160
430F	S43020	16–18	0.12	1.25	1.0	0.06	0.15¶	0.6 Mo	55 (379)	80 (552)	25	170
430FSe	S43023	16–18	0.12	1.25	1.0	0.06	0.06	0.15 Se¶	55 (379)	80 (552)	25	170
434	S43400	16–18	0.12	1.0	1.0	0.04	0.03	0.75–1.25 Mo	53 (365)	77 (531)	23	160
436	S43600	16–18	0.12	1.0	1.0	0.04	0.03	0.75–1.25 Mo (5 × C)(Cb + Ta)§	53 (365)	77 (531)	23	160
442	S44200	18–23	0.20	1.0	1.0	0.04	0.03		45 (310)	80 (552)	20	185
446	S44600	23–27	0.20	1.5	1.0	0.04	0.03	0.25N	55 (379)	85 (586)	25	160

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
†Single values are maximum values unless otherwise noted.
‡Typical temperature properties of annealed plates.
§0.70 maximum.
¶Minimum.

mal conductivity, and the materials can be damaged by thermal shock fairly easily. **Porcelain enamels** are used to coat steel, but the enamel has slightly inferior chemical resistance. Some refractory coatings, capable of taking very high temperatures, are also available.

Brick Construction Brick-lined construction can be used for many severely corrosive conditions under which high alloys would fail. Common bricks are made from carbon, red shale, or acidproof refractory materials. Red-shale brick is not used above 175°C (350°F) because of spalling. Acidproof refractories can be used up to 870°C (1,600°F).

A number of **cement** materials are used with brick. Standard are phenolic and furan resins, polyesters, sulfur, silicate, and epoxy-based materials. Carbon-filled polyesters and furanes are good against nonoxidizing acids, salts, and solvents. Silica-filled resins should not be used against hydrofluoric or fluosilicic acids. Sulfur-based cements are limited to 93°C (200°F), while resins can be used to about 180°C (350°F). The sodium silicate–based cements are good against acids to 400°C (750°F).

Differential thermal expansion of the brick, its joints, and the vessel substrate necessitates an intermediate lining of lead, asphalt, rubber,

TABLE 28-11 Standard Wrought Austenitic Stainless Steels*

AISI type	Composition, %† UNS	Cr	Ni	Mo	C	Si	Mn	Other	Mechanical properties‡ Yield strength, kip/in² (MPa)	Tensile strength' kip/in² (MPa)	Elongation, %	Hardness, HB
201	S20100	16–18	3.5–5.5		0.15	1.0	5.5–7.5	0.25 N	55 (379)	115 (793)	55	185
202	S20200	17–19	4–6		0.15	1.0	7.5–10.	0.25 N	55 (379)	105 (724)	55	185
301	S30100	16–18	6–8		0.15	1.0	2.0		40 (276)	105 (724)	55	165
302	S30200	17–19	8–10		0.15	1.0	2.0		35 (241)	90 (621)	60	150
302B	S30215	17–19	8–10		0.15	2.0–3.0	2.0		40 (276)	90 (621)	50	165
303	S30300	17–19	8–10	0.6	0.15	1.0	2.0	0.15 S,§ 0.2 P	35 (241)	90 (621)	50	160
303Se	S30323	17–19	8–10		0.15	1.0	2.0	0.15 Se,§ 0.2 P	35 (241)	90 (621)	50	160
304	S30400	18–20	8–10.5		0.08	1.0	2.0		35 (241)	82 (565)	60	149
304L	S30403	18–20	8–12		0.03	1.0	2.0		33 (228)	79 (545)	60	143
304N	S30451	18–20	8–10.5		0.08	1.0	2.0	0.10–0.16 N	48 (331)	90 (621)	50	180
308	S30800	19–21	10–12		0.08	1.0	2.0		30 (207)	85 (586)	55	150
309	S30900	22–24	12–15		0.20	1.0	2.0		40 (276)	95 (655)	45	170
309S	S30908	22–24	12–15		0.08	1.0	2.0		40 (276)	95 (655)	45	170
310	S31000	24–26	19–22		0.25	1.5	2.0		45 (310)	95 (655)	50	170
310S	S31008	24–26	19–22		0.08	1.5	2.0		45 (310)	95 (655)	50	170
314	S31400	23–26	19–22		0.25	1.5–3.0	2.0		50 (345)	100 (609)	45	180
316	S31600	16–18	10–14	2.0–3.0	0.08	1.0	2.0		36 (248)	82 (565)	55	149
316L	S31603	16–18	10–14	2.0–3.0	0.03	1.0	2.0		34 (234)	81 (558)	55	146
316N	S31651	16–18	10–14	2.0–3.0	0.08	1.0	2.0	0.10–0.16 N	42 (290)	90 (621)	55	180
317	S31700	18–20	11–15	3.0–4.0	0.08	1.0	2.0		40 (276)	85 (586)	50	160
317L	S31703	18–20	11–15	3.0–4.0	0.03	1.0	2.0		35 (241)	85 (586)	55	150
321	S32100	17–19	9–12		0.08	1.0	2.0	(5 × C) Ti§	30 (207)	85 (586)	55	160
329	S32900	25–30	3–6	1.0–2.0	0.10	1.0	2.0		80 (552)	105 (724)	25	230
347	S34700	17–19	9–13		0.08	1.0	2.0	(10 × C)(Cb + Ta)§	35 (241)	90 (621)	50	160
348	S34800	17–19	9–13		0.08	1.0	2.0	(10 × C)(Cb + Ta)¶ 0.20 Co	35 (241)	90 (621)	50	160

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
†Single values are maximum values unless otherwise noted.
‡Typical room-temperature properties of solution-annealed plates.
§Minimum.
¶Minimum except Ta = 0.1 maximum.

TABLE 28-12 Special Stainless Steels*

Alloy	UNS	Composition, %†							Mechanical properties‡			
		Cr	Ni	Mo	C	Mn	Si	Other	Yield strength, kip/in^2 (MPa)	Tensile strength, kip/in^2 (MPa)	Elongation, %	Hardness' HB
A-286	K66286	13.5–16	24–27	1.0–1.5	0.08	2.0	1.0	1.90–2.35 Ti, 0.1–0.5 V, 0.001–0.01 B, 8 × C–1.0 Cb	100 (690)	140 (970)	20	
20Cb-3	N08020	19–21	32–38	2.0–3.0	0.07	2.0	1.0	3.0–4.0 Cu	53 (365)	98 (676)	33	185
20Mod	N08320	21–23	25–27	4.0–6.0	0.05	2.5	1.0	(4.0 × C) Ti min.	43 (296)	84 (579)	42	160
PH13-8Mo	S13800	12.25–13.25	7.5–8.5	2.0–2.5	0.05	0.2	0.1	0.90–1.35 Al	120 (827)	160 (1100)	17	300
PH14-8Mo	S14800	13.75–15.0	7.75–8.75	2.0–3.0	0.05	1.0	1.0	0.75–1.5 Al, 0.15–45 Cb	55–210 (380–1450)	125–230 (860–1540)	2–25	200–450
15-5PH	S15500	14.0–15.5	3.5–5.5		0.07	1.0	1.0	2.5–4.5 Cu	145 (1000)	160 (1100)	15	320
PH15-7Mo	S15700	14.0–16.0	6.5–7.75	2.0–3.0	0.09	1.0	1.0	0.75–1.5 Al, 0.15–0.45 Cb	55–210 (380–1450)	130–220 (900–1520)	2–35	200–450
17-4PH	S17400	15.5–17.5	3.0–5.0		0.07	1.0	1.0	3.0–5.0 Cu, 0.4 Al	145 (1000)	160 (1100)	15	320
W	S17600	16.0–17.5	6.0–7.5		0.08	1.0	1.0	0.4–1.20 Ti	90–200 (620–1380)	135–210 (930–1450)	3–12	260–420
17-7PH	S17700	16.0–18.0	6.5–7.75		0.09	1.0	1.0	0.75–1.5 Al	40 (276)	130 (710)	10	185
216	S21600	17.5–22.0	5.0–7.0	2.0–3.0	0.08	7.5–9.0	1.0	0.25–0.5 N	70 (480)	115 (790)	45	200
Nitronic 60	S21800	16.0–18.0	8.0–9.0		0.10	7.0–9.0	3.5–4.5	0.08–0.18 N	60 (410)	103 (710)	62	210
21-6-9	S21900	18.0–21.0	5.0–7.0		0.08	8.0–10.0	1.0	0.15–0.40 N	68 (470)	112 (770)	44	220
AM350	S35000	16.0–17.0	4.0–5.0	2.5–3.25	0.07–0.11	0.5–1.25	0.5	0.07–0.13 N	60–173 (410–1200)	145–206 (1000–1420)	13.5–40	200–400
AM355	S35500	15.0–16.0	4.0–5.0	2.5–3.25	0.10–0.15	0.5–1.25	0.5		182 (1250)	216 (1490)	19	402–477
Almar 362	S36200	14.0–15.0	6.0–7.0		0.05	0.5	0.3	0.55–9.0 Ti	105–185 (124–286)	120–188 (827–1300)	15–13	250–400
18-18-2	S38100	17.0–19.0	17.5–18.5		0.08	2.0	1.5–2.5	0.20 × (C + N)	40 (280)	80 (550)	55	165
Stab. 18-2	S44400	17.5–19.5	1.0	1.75–2.5	0.025	1.0	1.0	min.–0.8 Ti + Cb 0.015 N	45 (310)	60 (414)	20	210
26-1	S44625	25.0–27.5	0.5	0.75–1.50	0.01	0.4	0.4	0.5 Ni + Cu	50 (345)	70 (480)	30	165
Stab. 26-1	S44626	25.0–27.0	0.5	0.75–1.50	0.06	0.75	0.75	7 × (C + Ni)–1.0 Ti, 0.15 Cu	50 (345)	70 (480)	30	165
28-4	S44700	28.0–30.0	0.15	3.5–4.2	0.010	0.3	0.2	0.02 N, 0.15 Cu	70 (480)	90 (620)	25	210
28-4-2	S44800	28.0–30.0	2.0–2.5	3.5–4.2	0.010	0.3	0.2	0.02 N, 8 × C Cb min.	85 (590)	95 (650)	25	230
Custom 450	S45000	14.0–16.0	5.0–7.0	0.5–1.0	0.05	1.0	1.0	1.25–1.75 Cu	117–184 (800–1270)	144–196 (990–1350)	14	270–400
Custom 455	S45500	11.0–12.5	7.5–9.5	0.5	0.05	0.5	0.5	1.5–2.5 Cu, 0.8–1.4 Ti	115–220 (790–1500)	140–230 (970–1600)	10–14	290–460

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in^2, multiply by 145.04.
†Single values are maximum values unless otherwise noted.
‡Typical room-temperature properties.

TABLE 28-13 Standard Cast Heat-Resistant Stainless Steels[a]

ACI	Equivalent AISI	UNS	Composition, %[b] Cr	Ni	C	Mn	Si	Other	Mechanical properties at 1600°F: Short term, Tensile strength, kip/in² (MPa)	Elongation, %	Stress to rupture in 1000 h, kip/in²	MPa
HA			8–10		0.2	0.35–0.65	1.0	0.9–1.2 Mo	44 (303)[c]	36[c]	27	186[d]
HC	446	J92605	26–30	4	0.5	1.0	2.0				1.3	9.0
HD	327	J93005	26–30	4–7	0.5	1.5	2.0		23 (159)	18	7.0	48[e]
HE		J93403	26–30	8–11	0.2–0.5	2.0	2.0					
HF	302B	J92603	18–23	9–12	0.2–0.4	2.0	2.0		21 (145)	16	4.4	30
HH[f]		J93503	24–28	11–14	0.2–0.5	2.0	2.0	0.2 N	18.5 (128)	30	3.8	26
HH[g]	309	J93503	24–28	11–14	0.2–0.5	2.0	2.0	0.2 N	21.5 (148)	18	3.8	26
HI		J94003	26–30	14–18	0.2–0.5	2.0	2.0		26 (179)	12	4.8	33
HK	310	J94224	24–28	18–22	0.2–0.6	2.0	2.0		23 (159)	16	6.0	41
HL		J94604	28–32	18–22	0.2–0.6	2.0	2.0		30 (207)			
HN		J94213	19–23	23–27	0.2–0.5	2.0	2.0		20 (138)	37	7.4	51
HP		J95705	24–28	33–37	0.35–0.75	2.0	2.5		26 (179)	27	7.5	52
HT	330	J94605	13–17	33–37	0.35–0.75	2.0	2.5		19 (131)	26	5.8	40
HU		J95405	17–21	37–41	0.35–0.75	2.0	2.5		20 (138)	20	5.2	36
HW			10–14	58–62	0.35–0.75	2.0	2.5		19 (131)		4.5	31
HX			15–19	64–68	0.35–0.75	2.0	2.5		20.5 (141)	48	4.0	28

[a] Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
[b] Single values are maximum values; S and P are 0.04 maximum; Mo is 0.5 maximum.
[c] At 1100°F (593°C).
[d] At 1000° (538°C).
[e] At 1400°F (760°C).
[f] Type I; partially ferritic.
[g] Type II; wholly austenitic.

TABLE 28-14 Standard Cast Corrosion-Resistant Stainless Steels[a]

ACI	Equivalent AISI	UNS	Composition, %[b] Cr	Ni	Mo	C	Mn	Si	Other	Mechanical properties[c]: Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation, %	Hardness, HB
Ca-15	410	J91150	11.5–14	1.0	0.5	0.15	1.00	1.50		150 (1034)[d]	200 (1379)[d]	7[d]	390[d]
CA-15M		J91151	11.5–14	1.0	0.15–1.0	0.15	1.00	1.50		150 (1034)[d]	200 (1379)[d]	7[d]	390[d]
CA-6NM		J91540	11.5–14	3.5–4.5	0.4–1.0	0.06	1.00	1.00		100 (690)[e]	120 (827)[e]	4[e]	269[e]
CA-40	420	J91153	11.5–14	1.0	0.5	0.20–0.40	1.00	1.50		165 (1138)[d]	220 (1517)[d]	1[d]	470[d]
CB-30	431	J91803	18.21	2.0		0.30	1.00	1.50		60 (414)[f]	95 (655)[f]	15[f]	195[f]
CC-50	446	J92615	26–30	4.0		0.50	1.00	1.50		65 (448)[g]	97 (669)[g]	18[g]	210[g]
CE-30	312	J93423	26–30	8–11		0.30	1.50	2.00		63 (434)	97 (669)	18	190
CB-7Cu	(17-4PH)		(16)	(4)		0.07			(3) Cu	165 (1138)		3	418
CD-4MCu			25–26.5	4.75–6.0	1.75–2.25	0.04	1.00	1.00	2.75–3.25 Cu	82 (565)	108 (745)	25	253
CF-3	304L	J92500	17–21	8–12		0.03	1.50	2.00		36 (248)	77 (531)	60	140
CF-8	304	J92600	18–21	8–11		0.08	1.50	2.00		37 (255)	77 (531)	55	140
CF-20	302	J92602	18–21	8–11		0.20	1.50	2.00		36 (248)	77 (531)	50	163
CF-3M	316L	J92800	17–21	9–13	2.0–3.0	0.03	1.50	1.50		38 (262)	80 (552)	55	150
CF-8M	316	J92900	18–21	9–12	2.0–3.0	0.08	1.50	2.00		42 (290)	80 (552)	50	160
CF-12M			18–21	9–12	2.0–3.0	0.12	1.50	2.00		42 (290)	80 (552)	50	160
CG-12	317	J93000	18–21	9–13	3.0–4.0	0.08	1.50	1.50		44 (303)	83 (572)	45	170
CF-8C	347	J92710	18–21	9–12		0.08	1.50	2.00	(8 × C) Cb[h]	38 (262)	77 (531)	39	149
CF-16F	303	J92701	18–21	9–12	1.50	0.16	1.50	2.00		40 (276)	77 (531)	52	150
CG-12		J93001	20–23	10–13		0.12	1.50	2.00		28 (193)		35	
CH-20	309	J93402	22–26	12–15		0.20	1.50	2.00		50 (345)	88 (607)	38	190
CK-20	310	J94202	23–27	19–22		0.20	1.50	2.00		38 (262)	76 (524)	37	144
CN-7M		J95150	19–22	27.5–30.5	2.0–3.0	0.07	1.50	1.50	3–4 Cu	32 (221)	69 (476)	48	130

[a] Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
[b] Single values are maximum values except those in parentheses, which are minimum values. P and S values are 0.04 maximum.
[c] Typical room-temperature properties for solution-annealed material unless otherwise noted.
[d] For material air-cooled from 1800°F and tempered at 600°F.
[e] For material air-cooled from 1750°F and tempered at 1100 to 1150°F.
[f] For material annealed at 1450°F, furnace-cooled to 1000°F, then air-cooled.
[g] Air-cooled from 1900°F.
[h] 1.0 maximum.

TABLE 28-15 Nickel Alloys*

Alloy	UNS	Composition, %†						Mechanical properties‡				
		NI(+Co)§	Cr	Fe	Mo	C	Other	Condition	Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation, %	Hardness, HB
200	N02200	99.		0.4		0.15		Annealed	15–30 (103–207)	55–80 (379–552)	55–40	90–120
201	N02201	99.		0.4		0.02		Annealed	10–25 (69–172)	50–60 (345–414)	60–40	75–102
400	N04400	63–70		1.0–2.5		0.3	28–34 Cu	Annealed	25–50 (172–345)	70–90 (483–621)	60–35	110–149
K-500	N05500	63–70		2.0		0.25	2.3–3.15 Al 0.35–0.85 Ti, 30 Cu	Age-hardened Annealed	85–120 (586–827)	130–165 (896–1138)	35–20	250–315
600	N06600	72.	14–17	6–10		0.15		Annealed	30–50 (207–345)	80–100 (552–690)	55–35	120–170
601	N06601	58–63	21–25	Bal.		0.10	1.0–1.7 Al	Annealed	30–60 (207–414)	80–115 (552–793)	70–40	110–150
625	N06625	Bal.	20–23	5	8–10	0.10	3.15–4.15 (Cb + Ta)	Annealed	60–95 (414–655)	120–150 (827–1034)	60–30	145–220
706	N09706	39–44	14.5–17.5	Bal.		0.06		Solution-treated and aged	161 (1110)	193 (1331)	20.	371.
718	N07718	50–55	17–21	Bal.	2.8–3.3	0.08	4.75–5.5 (Cb + Ta)	Special heat treatment	171 (1180)	196 (1351)	17.	382.
X-750	N07750	70	14–17	5–9		0.08	0.65–1.15 Ti, 0.2–0.8 Al 0.7–1.2 (Cb + Ta) 2.25–2.75 Ti, 0.4–1.0 Al	Special heat treatment	115–142 (793–979)	162–193 (1117–1331)	30–15	300–390
800	N08800	30–35	19–23	Bal.		0.10	0.15–0.6 Al, 0.15–0.6 Ti	Annealed	30–60 (207–414)	75–100 (517–690)	60–30	120–184
800H	N08800	30–35	19–23	Bal.		0.05–0.10	0.15–0.6 Al, 0.15–0.6 Ti	Solution-treated	20–50 (138–345)	65–95 (448–655)	50–30	100–184
801	N08801	30–34	19–22	Bal.		0.10	0.75–1.5 Ti	Special heat treatment	79.5 (548)	129 (889)	29.5	
825	N08825	38–46	19.5–23.5	Bal.	2.5–3.5	0.05	1.5–3.0 Cu, 0.6–1.2 Ti	Annealed	35–65 (241–448)	85–105 (586–724)	50–30	120–180
B-2	N10665	Bal.	1.0	2	26–30	0.02		Annealed	76 (524)	139 (958)	53.	210
C-276	N10276	Bal.	14.5–16.5	4–7	15–17	0.02	3.0–4.5 W	Annealed	52 (358)	115 (793)	61.	194
C-4	N06455	Bal.	14–18	3	14–17	0.015	0.7 Ti	Annealed	61 (421)	116 (800)	54.	194
G	N06007	Bal.	21–23	18–21	5.5–7.5	0.05	1.0–2.0 Mn, 1.5–2.5 Cu 1.75–2.5 (Cb + Ta)	Annealed	46 (317)	102 (703)	61.	161
X	N06002	Bal.	20.5–23	17–20	8–10	0.05–0.15	0.2–1.0 W	Annealed	56 (386)	110 (758)	45.	178

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
†Single values are maximum unless otherwise noted.
‡Typical room-temperature properties.
§Single values are minima.

TABLE 28-16 Aluminum Alloys

AA designation	UNS	Composition, %*						Condition‡	Mechanical properties†			
		Cr	Cu	Mg	Mn	Si	Other		Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation in 2 in, %	Hardness' HB
Wrought												
1060	A91060						99.6 Al min.	0	4 (28)	10 (69)	43	19
1100	A91100		0.05–0.2				99.0 Al min.	0	5 (34)	13 (90)	45	23
2024	A92024	0.1	3.8–4.9	1.2–1.8	0.3–0.9	0.5		T4	47 (324)	68 (469)	19	120
3003	A93003		0.05–0.2		1.0–1.5	0.6		H14	21 (145)	22 (152)	16	40
5052	A95052	0.15–0.35	0.1	2.2–2.8	0.1			0	13 (90)	2.8 (193)	30	47
5083	A95083	0.05–0.25	0.1	4.0–4.9	0.4–1.0	0.4		0	21 (145)			
5086	A95086	0.05–0.25	0.1	3.5–4.5	0.2–0.7	0.4		0	17 (117)	38 (262)	30	
5154	A95154	0.05–0.35	0.1	3.1–3.9	0.1	0.25		0	17 (117)	35 (241)	27	58
6061	A96061	0.04–0.35	0.15–0.4	0.8–1.2	0.15	0.4–0.8		T6	40 (276)	45 (310)	17	95
6063	A96063	0.1	0.1	0.45–0.9	0.1	0.2–0.6		T6	31 (214)	35 (241)	18	73
7075	A97075	0.18–0.28	1.2–2.0	2.1–2.9	0.3	0.40	5.1–6.1 Zn	T6	73 (503)	63 (572)	11	150
Cast												
242.0	A02420	0.25	3.5–4.5	1.2–1.8	0.35	0.7	1.7–2.3 Ni	S-T571		29 (200)		
295.0	A02950		4.0–5.0	0.03	0.35	0.7–1.5		S-T4		29 (200)	6	
A332.0	A13320		0.5–1.5	0.7–1.3	0.35	11–13	2.0–3.0 Ni	P-T551		31 (214)		
B443.0	A24430		0.15	0.05	0.35	4.5–6.0		S-F		17 (117)	3	
514.0	A05140		0.15	3.5–4.5	0.35	0.35		S-F		22 (152)	6	
520.0	A05200		0.25	9.5–10.6	0.15	0.25		S-T4	22 (152)	42 (290)	12	

*Single values are maximum values.
†Typical room-temperature properties.
‡S = sand-cast; P = permanent-mold-cast; other = temper designations.
SOURCE: Aluminum Association. Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.

or plastic. This membrane functions as a barrier to protect the substrate from corrosion damage. A special prestressed-brick design that maintains the brick in compression by using a controlled-expansion resinous mortar and brick bedding material precludes the use of an elastomeric membrane.

Cement and Concrete Concrete is an aggregate of inert reinforcing particles in an amorphous matrix of hardened cement paste. Concrete made of portland cement has limited resistance to acids and bases and will fail mechanically following absorption of crystal-forming solutions such as brines and various organics. Concretes made of corrosion-resistant cements (such as calcium aluminate) can be selected for specific chemical exposures.

Soil Clay is the primary construction material for settling basins and waste-treatment evaporation ponds. Since there is no single type of clay even within a given geographical area, shrinkage, porosity, absorption characteristics, and chemical resistance must be checked for each application.

ORGANIC NONMETALLICS

Plastic Materials In comparison with metallic materials, the use of plastics is limited to relatively moderate temperatures and pressures [230°C (450°F) is considered high for plastics]. Plastics are also less resistant to mechanical abuse and have high expansion rates, low strengths (thermoplastics), and only fair resistance to solvents. However, they are lightweight, are good thermal and electrical insulators, are easy to fabricate and install, and have low friction factors.

Generally, plastics have excellent resistance to weak mineral acids and are unaffected by inorganic salt solutions—areas where metals are not entirely suitable. Since plastics do not corrode in the electrochemical sense, they offer another advantage over metals: most metals are affected by slight changes in pH, or minor impurities, or oxygen content, while plastics will remain resistant to these same changes.

The important thermoplastics used commercially are polyethylene, acrylonitrile butadiene styrene (ABS), polyvinyl chloride (PVC), cellulose acetate butyrate (CAB), vinylidene chloride (Saran), fluorocarbons (Teflon, Halar, Kel-F, Kynar), polycarbonates, polypropylene, nylons, and acetals (Delrin). Important thermosetting plastics are general-purpose polyester glass reinforced, bisphenol-based polyester glass, epoxy glass, vinyl ester glass, furan and phenolic glass, and asbestos reinforced.

THERMOPLASTICS

The most chemical-resistant plastic commercially available today is **tetrafluoroethylene** or **TFE** (Teflon). This thermoplastic is practically unaffected by all alkalies and acids except fluorine and chlorine gas at elevated temperatures and molten metals. It retains its properties up to 260°C (500°F). **Chlorotrifluoroethylene** or **CTFE** (Kel-F, Plaskon) also possesses excellent corrosion resistance to almost all acids and alkalies up to 180°C (350°F). A Teflon derivative has been developed from the copolymerization of tetrafluoroethylene and hexafluoropropylene. This resin, **FEP,** has similar properties to TFE except that it is not recommended for continuous exposures at temperatures above 200°C (400°F). Also, FEP can be extruded on conventional extrusion equipment, while TFE parts must be made by complicated powder-metallurgy techniques. Another version is **polyvinylidene fluoride,** or **PVF_2** (Kynar), which has excellent resistance to alkalies and acids to 150°C (300°F). It can be extruded. A more recent development is a copolymer of CTFE and ethylene (Halar). This material has excellent resistance to strong inorganic acids, bases, and salts up to 150°C. It also can be extruded.

Perfluoroalkoxy, or **PFA** (Teflon), has the general properties and chemical resistance of FEP at a temperature approaching 300°C (600°F).

Polyethylene is the lowest-cost plastic commercially available. Mechanical properties are generally poor, particularly above 50°C (120°F), and pipe must be fully supported. Carbon-filled grades are resistant to sunlight and weathering.

Unplasticized polyvinyl chlorides (type I) have excellent resistance to oxidizing acids other than concentrated and to most nonoxidizing acids. Resistance is good to weak and strong alkaline materials. Resistance to chlorinated hydrocarbons is not good. Polyvinylidene chloride, known as **Saran,** has good resistance to chlorinated hydrocarbons.

Acrylonitrile butadiene styrene (**ABS**) polymers have good resistance to nonoxidizing and weak acids but are not satisfactory with oxidizing acids. The upper temperature limit is about 65°C (150°F).

TABLE 28-17 Copper Alloys*

Alloy	CDA	UNS	Composition, %†						Mechanical properties‡		
			Cu	Zn	Sn	Al	Ni	Other	Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation in 2 in, %
Wrought											
Copper	110	C11000	99.90						10 (69)	32 (221)	55
Commercial bronze	220	C22000	89–91	Rem.					10 (69)	37 (255)	50
Red brass	230	C23000	84–86	Rem.					10 (69)	40 (276)	55
Cartridge brass	260	C26000	68.5–71.5	Rem.					11 (76)	44 (303)	66
Yellow brass	270	C27000	63–68.5	Rem.					14 (97)	46 (317)	65
Muntz Metal	280	C28000	59–63	Rem.					21 (145)	54 (372)	52
Admiralty brass	443	C44300	70–73	Rem.	0.9–1.2			0.02–0.1 As	18 (124)	48 (331)	65
Admiralty brass	444	C44400	70–73	Rem.	0.9–1.2			0.02–0.1 Sb	18 (124)	48 (331)	65
Admiralty brass	445	C44500	70–73	Rem.	0.9–1.2			0.02–0.1 P	18 (124)	48 (331)	65
Naval brass	464	C46400	59–62	Rem.	0.5–1.0				25 (172)	58 (400)	50
Phosphor bronze	510	C51000	Rem.	0.3	4.2–5.8			0.03–0.35 P	19 (131)	47 (324)	64
Phosphor bronze	524	C52400	Rem.	0.2	9.0–11.0			0.03–0.35 P	28 (193)	66 (455)	70
Aluminum bronze	613	C61300	86.5–93.8		0.2–0.5	6–8	0.5	3.5 Fe	30 (207)	70 (483)	42
Aluminum bronze D	614	C61400	88.0–92.5	0.2		6–8		1.5–3.5 Fe, 1.0 Mn	33 (228)	76 (524)	45
Nickel-aluminum bronze	630	C63000	78–85	0.3	0.2	9–11	4.0–5.5	2.0–4.0 Fe, 1.5 Mn, 0.25 Si	36 (248)	90 (620)	10
High-silicon bronze	655	C65500	94.8	1.5			0.6	0.8 Fe, 0.5–1.3 Mn, 2.8–3.8 Si	21 (145)	56 (386)	63
Manganese bronze	675	C67500	57–60	Rem.	0.5–1.5	0.25		0.05–0.5 Mn, 0.8–2.0 Fe	30 (207)	65 (448)	33
Aluminum brass	687	C68700	76–79	Rem.		1.8–2.5		0.02–0.1 As	27 (186)	60 (414)	55
90-10 copper nickel	706	C70600	86.5	1.0			9.0–11.0	1.0–1.8 Fe, 1.0 Mn	16 (110)	44 (303)	42
70-30 copper nickel	715	C71500	Rem.	1.0			29–33	0.4–1.0 Fe, 1.0 Mn	20 (138)	54 (372)	45
65-18 nickel silver	752	C75200	63–66.5	Rem.			16.5–19.5	0.25 Fe, 0.5 Mn	25 (172)	56 (386)	45
Cast											
Ounce metal	836	C83600	84–86	4–6	4–6	0.005	1.0	4–6 Pb	17 (117)	37 (255)	30
Manganese bronze	865	C86500	55–65	36–42	1.0	0.5–1.5	1.0	0.4–2.0 Fe 0.1–1.5 Mn	28 (193)	71 (490)	30
G bronze	905	C90500	86–89	1.0–3.0	9–11	0.005	1.0		22 (152)	45 (310)	25
M bronze	922	C92200	86–90	3.0–5.0	5.5–6.5	0.005	1.0	1.0–2.0 Pb	20 (138)	40 (276)	30
Ni-Al-Mn bronze	957	C95700	71			7.0–8.5	1.5–3.0	2.0–4.0 Fe 11–14 Mn	45 (310)	95 (665)	26
Ni-Al bronze	958	C95800	79			8.5–9.5	4.0–5.0	3.5–4.5 Fe 0.8–1.5 Mn	38 (262)	95 (655)	25
Copper nickel	964	C96400	65–69				28–32	0.5–1.5 Cb 0.25–1.5 Fe, 1.5 Mn	37 (255)	68 (469)	28

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
†Single values are maximum values except for Cu, which is minimum.
‡Typical room-temperature properties of annealed or as-cast material.

Acetals have excellent resistance to most organic solvents but are not satisfactory for use with strong acids and alkalies.

Cellulose acetate butyrate is not affected by dilute acids and alkalies or gasoline, but chlorinated solvents cause some swelling. **Nylons** resist many organic solvents but are attacked by phenols, strong oxidizing agents, and mineral acids.

Polypropylene has a chemical resistance about the same as that of polyethylene, but it can be used at 120°C (250°F). **Polycarbonate** is a relatively high-temperature plastic. It can be used up to 150°C (300°F). Resistance to mineral acids is good. Strong alkalies slowly decompose it, but mild alkalies do not. It is partially soluble in aromatic solvents and soluble in chlorinated hydrocarbons. **Polyphenylene oxide** has good resistance to aliphatic solvents, acids, and bases but poor resistance to esters, ketones, and aromatic or chlorinated solvents.

Polyphenylene sulfide (**PPS**) has no known solvents below 190 to 205°C (375 to 400°F); mechanical properties of PPS are unaffected by exposures in air at 230°C (450°F). It is resistant to aqueous inorganic salts and bases.

Polysulfone can be used to 170°C (340°F); it is highly resistant to mineral acid, alkali, and salt solutions as well as to detergents, oils, and alcohols. It is attacked by such organic solvents as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons.

Polyamide or polyimide polymers are resistant to aliphatic, aromatic, and chlorinated or fluorinated hydrocarbons as well as to many acidic and basic systems but are degraded by high-temperature caustic exposures.

Thermosetting Plastics Among the thermosetting materials are phenolic plastics filled with asbestos, carbon or graphite, glass, and silica. Relatively low cost, good mechanical properties, and chemical resistance (except against strong alkalies) make phenolics popular for chemical equipment. Furan plastics filled with asbestos and glass have much better alkali resistance than phenolic resins. They are more expensive than the phenolics but also offer somewhat higher strengths.

Polyester resins, reinforced with fiberglass, have good strength and good chemical resistance except to alkalies. Some special materials in this class, based on bisphenol and vinyl esters are more alkali-

TABLE 28-18 Typical Mechanical Properties of Selected Materials

Material	Tensile modulus, GPa	Tensile strength, yield, MPa	Tensile strength, ultimate, MPa	Elongation, %	Poisson's ratio	Fracture toughness, MPa$\sqrt{m}$
High-nickel gray cast iron						
20°C	79–130		170–310			
500°C			130–212			
700°C			60–115			
Medium-silicon ductile cast iron						
295°C		210–240	415–690	0.2		
Low-carbon steel sheet				In 50 mm		
20°C Hot rolled		27–48	40–66	25–43		
20°C Cold rolled		23–37	43–56	30–44		
SA-335P12 (ASME) ferritic steel				In 50 mm		
20°C	200	207	415	30(L), 20(T)	0.288	
540°C	155	170	345		0.303	
Type 4330V low-alloy steel				In 50 mm		
Oil-quenched plate						
20°C	200	1150	1330	13		130
Type 301 stainless steel				In 50 mm		
−100°C Annealed	196	410	1300			
20°C	190	205	515	30		214
650°C	80	100	260	34		225
Type 304 stainless steel				In 50 mm		
−200°C Annealed bar	204	280	1400–1520	32–45		
20°C	190	350–560	660–770	45–72	0.26	
400°C	168	245–475	525–610	26–48	0.32	
800°C	120	210–280	245–350	22–60		
Type 316 stainless steel				In 50 mm		
−200°C Annealed	232		1440	60 (25 mm)	0.281	
20°C	196	250	560	64	0.294	
400°C	167	170	500	48	0.331	
800°C	130	120	200	42	0.265	
Type 347 stainless steel				In 50 mm		
−200°C Annealed bar		430	1500	43		
20°C	200	380	670	50	0.30	
400°C	170	150–180	460	34	0.32	
800°C	105	110	160	42	0.25	
Alloy 42 (Fe + 42Ni)						
20°C	143	286	492	33.5	0.34	
100°C	150	222	445	41.3	0.33	
175°C	165	182	408	29.6	0.32	
250°C	174	152	388	34.6	0.30	
Kovar (Fe + 29Ni + 17Co)						
20°C	134	372	526	31.5	0.37	
100°C	139	295	454	30	0.36	
175°C	149	235	418	36	0.35	
250°C	153	192	396	35	0.33	
63Sn + 37Pb						
−70°C	34	60	85			
20°C	31	38	53	35		
125°C		18	25	48		
150°C		15	15	105		
Aluminum						
−200°C Annealed	76	61	184	13	0.34	
20°C	70	37	184	19.5	0.35	
400°C	58	5.5	18	19.5	0.36	
600°C	49		9.2		0.38	
Antimony						
20°C	77.7		11.40			
Beryllium, grade S-200 F						
20°C	303	262–269	380–413	2–5		9–13
400°C		255–262	317–331	11–26		
1000°C		138–145	186–200	6–10		
Bismuth						
20°C	32					
Cadmium				In 25 mm		
20°C	55		69–83	50	0.33	
Chromium (electrolytic)				In 25 mm		
20°C	248		83	0		
400°C	227	140	225	51		
800°C	255	97	180	47		
Cobalt				In 50 mm		
20°C Annealed	211		255.1			
Zone-refined		758.5	944.6			
Annealed strip		310–345		15–22		

TABLE 28-18 Typical Mechanical Properties of Selected Materials (*Continued*)

Material	Tensile modulus, GPa	Tensile strength, yield, MPa	Tensile strength, ultimate, MPa	Elongation, %	Poisson's ratio	Fracture toughness, MPa$\sqrt{m}$
Copper						
–200°C Annealed	137	96	360	46	0.336	
20°C	128	71	212	51	0.344	
100°C	125	71	181	53	0.346	
300°C		70	128	56		
400°C	112				0.353	
500°C	107				0.358	
–200°C Cold worked		200	390–517			
20°C		170	230–393			
100°C		160	205–381			
200°C		140	175–350			
600°C			46			
20°C Cast			145			
100°C			120			
200°C			98			
600°C			37			
Gold						
20°C	78		103	30		
Iron						
–200°		320–480				
20°C	208.2	70–140			0.291	
Lead						
–200°C Annealed	24					
20°C	18.8		12	68		
100°C	16.7		8	74		
150°C			5.5	86		
Magnesium (annealed sheet)				In 50 mm		
20°C	40	90–105	160–195	3–15		
Manganese (γ phase)						
20°C	191	241	496	40		
Molybdenum						
–100°C		650–750				
20°C	315	310–385	550–650			
500°C	285	110	250–315			
1200°C	215		100–140			
Tin						
–200°C Annealed	61					
20°C	50		24–38	33	0.33	
100°C	43.5		12–19	41		
150°C			8–10	50		
Titanium				In 50 mm		
20°C	105	140	235	54		
400°C	80		105	41		
Tungsten, annealed						
20°C	407–410					
400°C	393–396	75–130	275–355	33–58		
1800°C	322–325	6–42	35–85	19–43		
Teflon (PTFE)						
–200°C	5.5	111	112			
20°C	0.86	13	30			
100°C	0.23	7	10			
250°C		3	1.2			
Kapton						
–200°C	5.2	236 (L)	360		0.275	
20°C	3.9	105	212	72	0.365	8–10
100°C	3.1	87	161		0.441	6.3–8.8
200°C	1.3	80	117		0.568	
Kevlar 49	L T					
20°C	126,6.9		3480	2.9	0.36	
100°C	114,16.6		3200	2.8	0.36	
200°	110		2800			
Amoco P75/ERLX 1962 $[0]_8$ unidirectional laminate				Strain-to-Failure		
20°C	46		120	0.26		
S-glass/Epoxy 2D (0)	Hercules 3501-6		Shell Epon (828 & 1031)			
–100°C 0° Orientation	60					
20°C	57–80		1600			
100°C	50–62		1350–1600			
20°C 90° Orientation	12–22					
100°C	5–19					

TABLE 28-18 Typical Mechanical Properties of Selected Materials (*Concluded*)

Material	Tensile modulus, GPa	Tensile strength, yield, MPa	Flexural strength, MPa	Poisson's ratio	Fracture toughness, MPa√m
Alumina (>99%)					
20°C	401	275–1030	520	0.24	3.2–4.0
600°C	343		360	0.25	
1200°C			340	0.35	
1400°C			260		
Silicon nitride					
20°C Sintered	248 (195–315)		415 (275–840)	0.28	4.66 (4.40–5.40)
1400°C			70 (0–700)	0.26	4.70 (3.40–6.80)
20°C Hot pressed	314 (250–325)	375	750 (450–1100)		
1000°C	300		600		
1400°C	175 (175–250)	150	300 (0–600)		
Silicon carbide					
20°C Hot pressed	450 (430–450)	200	470	0.17	3.85 (3–4)
800°C			412		
1000°C			227		3.59
1200°C			324		3.52
1400°C	380	35–150	175 (175–525)		2.81
20°C Sintered	411 (375–420)		460	0.16	3.01 (2.5–6.5)
800°C			326	0.165	
1000°C			353	0.170	
1200°C			377	0.192	
1400°C	372		240		
Boron nitride (H)	L T		L T		
20°C Hot pressed	92,36		120,51		
100°C	84,34		116,50		
400°C	61,27		105,44		
400°C	24,10		60,12		
Aluminum nitride					
20°C Hot pressed	345		390		2.90 (2.90–3.40)
700°C	343		375		2.80
1050°C			267		3.30
Silicon					
20°C	130 [100]	2900	2800–3100		0.76
400°C		200			
800°C		23			
1000°C		7.5			
1200°C		2.5			
Silica					
–200°C Fused	68				
20°C	71	49	66	0.17	
400°C	76				
900°C	82				

SOURCE: Center for Information and Numerical Data Analysis and Synthesis (CINDAS), Purdue University, West Lafayette, Ind.

resistant. The temperature limit for polyesters is about 90 to 150°C (200 to 300°F), depending upon exposure conditions.

Epoxies reinforced with fiberglass have very high strengths and resistance to heat. The chemical resistance of the epoxy resin is excellent in nonoxidizing and weak acids but not good against strong acids. Alkaline resistance is excellent in weak solutions. Resistance is poor to such organic solvents as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons.

The thermoset polyimides are a family of heat-resistant polymers with acceptable properties up to 260°C (500°F). They are unaffected by dilute acids, aromatic and aliphatic hydrocarbons, esters, ethers, and alcohols but are attacked by dilute alkalies and concentrated inorganic acids.

Chemical resistance of thermosetting-resin-glass-reinforced laminates may be affected by any exposed glass in the laminate.

Phenolic asbestos, general-purpose polyester glass, Saran, and CAB are adversely affected by alkalies. And thermoplastics generally show poor resistance to organics.

The lack of homogeneity and the friable nature of FRP composite structures dictate that caution be followed in mechanical design, vendor selection, inspection, shipment, installation, and use.

FRP code vessels for pressure service over 0.1 MPA (15 lbf/in^2) may be designed and built under ASME Sec. X. Equipment for service from full vacuum through 0.1-MPA (15-lbf/in^2) pressure, while not presently covered by an ASME code designation, can be designed or fabricated in accordance with the SPI-MTI Quality Assurance Practices and Procedures Report for RTP equipment.

Rubber and Elastomers Rubber and elastomers are widely used as lining materials. To meet the demands of the chemical industry, rubber processors are continually improving their products. A number of synthetic rubbers have been developed, and while none has all the properties of natural rubber, they are superior in one or more ways. The isoprene and polybutadiene synthetic rubbers are duplicates of natural.

The ability to bond natural rubber to itself and to steel makes it ideal for lining tanks. Many of the synthetic elastomers, while more chemically resistant than natural rubber, have very poor bonding characteristics and hence are not well suited for lining tanks.

Natural rubber is resistant to dilute mineral acids, alkalies, and salts, but oxidizing media, oils, and most organic solvents will attack it. **Hard rubber** is made by adding 25 percent or more of sulfur to natural or synthetic rubber and, as such, is both hard and strong. **Chloroprene** or **neoprene rubber** is resistant to attack by ozone, sunlight, oils, gasoline, and aromatic or halogenated solvents but is easily permeated by water, thus limiting its use as a tank lining. **Styrene rubber** has chemical resistance similar to that of natural. **Nitrile rubber** is known for resistance to oils and solvents. **Butyl rubber**'s resistance to dilute mineral acids and alkalies is exceptional; resistance to concen-

TABLE 28-19 Miscellaneous Alloys*

Alloy	Designation	UNS	Composition, %‡	Condition	Mechanical properties†			
					Yield strength, kip/in² (MPa)	Tensile strength, kip/in² (MPa)	Elongation, %	Hardness, HB
Refractory alloys								
Niobium R04210 (columbium)		204–210	99.6 Cb	Annealed	37 (255)	53 (365)	26	80
Molybdenum		R03600	0.01–0.04 C					
Molybdenum, low C		R03650	0.01 C					
Molybdenum alloy		R03630	0.01–0.04 C, 0.40–0.55 Ti, 0.06–0.12 Zn					
Tantalum		R05200	99.8 min. Ta	Annealed		50 (345)	40	45
Tungsten		R07030	99.9 min. W	Annealed		270 (1862)		
Zirconium		R60702	4.5 Hf, 0.2 Fe + Cr, 99.2 Zi + Hf	Annealed	16 (110)	36 (248)	31	77
Precious metals and alloys								
Gold		P00020	99.95 min. Au	Annealed		19 (131)	45	25
Silver		P07015	99.95 min. Ag	Annealed	8 (55)	18 (124)	54	27
Sterling silver			7.5 Cu, 92.5 Ag	Annealed	20 (138)	41 (283)	26	65
Platinum		P04955	99.95 min. Pt	Annealed		18 (124)	38	39
Palladium		P03980	99.80 min. Pd	Annealed		25 (172)	27	38
Lead alloys								
Chemical lead			99.9 min. Pb	Rolled	1.9 (13)	2.5 (17)	50	5
Antimonial lead			90 Pb, 10 Sb	Rolled		4.1 (28)	47	13
Tellurium lead			99.85 Pb, 0.04 Te, 0.06 Cu	Rolled	2.2 (15)	3 (21)	45	6
50-50 solder		L05500	50 Pb, 50 Sn, 0.12 max. Sb	Cast		6.8 (47)	50	14
Magnesium alloys								
Wrought alloy	AZ31B	M11311	2.5–3.5 Al, 0.20 min. Mn, 0.6–1.4 Zn	Annealed	15–18 (103–124)	32 (220)	9–12	56
Cast alloy	AZ91C	M11914	8.1–9.3 Al, 0.13 min. Mn, 0.4–1.0 Zn	As cast	11 (76)	23 (159)		60
Cast alloy	EZ33A	M12330	2.0–3.1 Zn, 0.5–1.0 Zr	Aged	14 (97)	20 (138)	2	50
Wrought alloy	HK31A	M13310	0.3 Zn, 2.5–4.0 Th, 0.4–1.0 Zr	Stress hard-annealed	24–26 (165–179)	33–34 (228–234)	4	57
Titanium alloys								
Commercial pure	Gr. 1	R50250	0.20 Fe, 0.18 O	Annealed	35 (241)	48 (331)	30	120
Commercial pure	Gr. 2	R50400	0.30 Fe, 0.25 O	Annealed	50 (345)	63 (434)	28	200
Ti-Pd	Gr. 7	R52400	0.30 Fe, 0.25 O, 0.12–0.25 Pd	Annealed	50 (345)	63 (434)	28	200
Ti-6Al-4V	Gr. 5	R56400	5.5–5.6 Al, 0.40 Fe, 0.20 O, 3.5–4.5 V	Annealed	134 (924)	144 (993)	14	330
Low alloy	Gr. 12		0.2–0.4 Mo, 0.6–0.9 Ni	Annealed	65 (448)	75 (517)	25	
Cobalt alloys								
	N-155	R30155	0.08–0.16 C, 0.75–1.25 Cb, 18.50–21.0 Co, 20.0–22.5 Cr, 1.0–2.0 Mn, 2.5–3.5 Mo, 19–21 Ni, 1.0 Si, 2.0–3.0 W					
	MP35N	R30036	0.025 C, 19–21 Cr, 1.0 Fe, 0.15 Mn, 9.0–10.5 Mo, 33.37 Ni, 0.15 Si, 1.0 Ti	Annealed	60 (414)	135 (931)	70	
	Stelite 6	R30006	0.9–1.4 C, 27–31 Cr, 3 Fe, 1.0 Mn, 1.5 Mo, 3.0 Ni, 1.5 Si, 3.5–5.5 W	As cast		105 (724)	1	

*Courtesy of National Association of Corrosion Engineers. To convert MPa to lbf/in², multiply by 145.04.
†Typical room-temperature properties.
‡Single values are maximum values unless otherwise noted.

TABLE 28-20 Properties of Glass and Silica*

	Pyroceram	96% silica	Borosilicate	Glass lining
Specific gravity, 77°F	2.60	2.18	2.23	2.56
Water absorption, %	0.00	0.00	0.00	
Gas permeability	Gastight	Gastight	Gastight	
Softening temperature, °F (°C)	2282 (1250)	2732 (1500)	1508 (1820)	
Specific heat, 77°F Btu/(lb·°F)[J/(kg·K)]	0.185 (775)	0.178 (746)	0.186 (779)	
Mean specific heat (77–752°F)	0.230	0.224	0.233	
Thermal conductivity, mean temperature, 77°F, Btu/(ft²·h·°F)/in [W/(m·K)]	25.2 (3.6)		7.5 (1.1)	
Linear thermal expansion, per °F (77–572°F); (per °C), × 10^{-6}	3.2 (5.8)	0.44 (0.79)	1.8 (3.2)	
Modulus of elasticity, kip/in² (MPa) × 10^3	17.3 (119)	9.6 (66)	9.5 (66)	6–9 (40–60)
Poisson's ratio	0.245	0.17	0.20	
Modulus of rupture, kip/in²	20 (140)	5–9 (35–63)	6–10 (42–70)	
Knoop hardness, 100 g	698	532	481	480
Knoop hardness, 500 g	619	477	442	
Adhesion strength kip/in² (MPa)				5–10 (35–70)
Maximum operating temperature, °F (°C)				500 (260)
Thermal shock resistance, temperature difference, °F (°C)				305 (152)

*Courtesy of National Association of Corrosion Engineers.

trated acids, except nitric and sulfuric, is good. **Silicone rubbers,** also known as polysiloxanes, have outstanding resistance to high and low temperatures as well as against aliphatic solvents, oils, and greases. **Chlorosulfonated polyethylene,** known as **Hypalon,** has outstanding resistance to ozone and oxidizing agents except fuming nitric and sulfuric acids. Oil resistance is good. **Fluoroelastomers** (**Viton A, Kel-F, Kalrez**) combine excellent chemical and temperature resistance. **Polyvinyl chloride elastomer** (**Koroseal**) was developed to overcome some of the limitations of natural and synthetic rubbers. It has excellent resistance to mineral acids and petroleum oils.

The **cis-polybutadiene, cis-polyisoprene,** and **ethylene-propylene** rubbers are close duplicates of natural rubber. The newer ethylene-propylene rubbers (EPR) have excellent resistance to heat and oxidation.

Asphalt Asphalt is used as a flexible protective coating, as a brick-lining membrane, and as a chemical-resisting floor covering and road surface. Resistant to acids and bases, alphalt is soluble in organic solvents such as ketones, most chlorinated hydrocarbons, and aromatic hydrocarbons.

Carbon and Graphite The chemical resistance of impervious carbon and graphite depends somewhat on the type of resin impregnant used to make the material impervious. Generally, impervious graphite is completely inert to all but the most severe oxidizing conditions. This property, combined with excellent heat transfer, has made impervious carbon and graphite very popular in heat exchangers, as brick lining, and in pipe and pumps. One limitation of these materials is low tensile strength. Threshold oxidation temperatures are 350°C (660°F) for carbon and 400°C (750°F) for graphite.

TABLE 28-21 Chemical Resistance of Important Plastics

	Polypropylene polyethylene	CAB*	ABS†	PVC‡	Saran§	Polyester glass¶	Epoxy glass	Phenolic asbestos	Fluorocarbons	Chlorinated polyether (Penton)	Polycarbonate
10% H_2SO_4	Excel.	Good	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.
50% H_2SO_4	Excel.	Poor	Excel.	Excel.	Excel.	Good	Excel.	Excel.	Excel.	Excel.	Excel.
10% HCl	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.
10% HNO_3	Excel.	Poor	Good	Excel.	Excel.	Good	Good	Fair	Excel.	Excel.	Excel.
10% Acetic	Excel.	Good	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.
10% NaOH	Excel.	Fair	Excel.	Good	Fair	Fair	Excel.	Poor	Excel.	Excel.	Excel.
50% NaOH	Excel.	Poor	Excel.	Excel.	Fair	Poor	Good	Poor	Excel.	Excel.	Excel.
NH_4OH	Excel.	Poor	Excel.	Excel.	Poor	Fair	Excel.	Poor	Excel.	Excel.	Excel.
NaCl	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.
$FeCl_3$	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.
$CuSO_4$	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.
NH_4NO_3	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Good	Excel.	Excel.	Excel.
Wet H_2S	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	
Wet Cl_2	Poor	Poor	Excel.	Good	Poor	Poor	Poor	Excel.	Excel.	Excel.	
Wet SO_2	Excel.	Poor	Excel.	Excel.	Good	Excel.	Excel.	Excel.	Excel.	Excel.	
Gasoline	Poor	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.
Benzene	Poor	Poor	Poor	Poor	Fair	Good	Excel.	Excel.	Excel.	Fair	Fair
CCl_4	Poor	Poor	Poor	Fair	Fair	Excel.	Good	Excel.	Excel.	Fair	Poor
Acetone	Poor	Poor	Poor	Poor	Fair	Poor	Good	Poor	Excel.	Good	Good
Alcohol	Poor	Poor	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.	Excel.

NOTE: Ratings are for long-term exposures at ambient temperatures [less than 38°C (100°F)].
*Cellulose acetate butyrate.
†Acrylonitrile butadiene styrene polymer.
‡Polyvinyl chloride, type I.
§Chemical resistance of Saran-lined pipe is superior to extruded Saran in some environments.
¶Refers to general-purpose polyesters. Special polyesters have superior resistance, particularly in alkalies.

Several types of resin impregnates are employed in manufacturing impervious graphite. The standard impregnant is a phenolic resin suitable for service in most acids, salt solutions, and organic compounds. A modified phenolic impregnant is recommended for service in alkalies and oxidizing chemicals. Furan and epoxy thermosetting resins are also used to fill structural voids. The chemical resistance of the impervious graphite is controlled by the resin used. However, no type of impervious graphite is recommended for use in over 60 percent hydrofluoric, over 20 percent nitric, and over 96 percent sulfuric acids and in 100 percent bromine, fluorine, or iodine.

Wood While fairly inert chemically, wood is readily dehydrated by concentrated solutions and hence shrinks badly when subjected to the action of such solutions. It is also slowly hydrolyzed by acids and alkalies, especially when hot. In tank construction, if sufficient shrinkage once takes place to allow crystals to form between the staves, it becomes very difficult to make the tank tight again.

A number of manufacturers offer wood impregnated to resist acids or alkalies or the effects of high temperatures.

HIGH- AND LOW-TEMPERATURE MATERIALS

LOW-TEMPERATURE METALS

The low-temperature properties of metals have created some unusual problems in fabricating cryogenic equipment.

Most metals lose their ductility and impact strength at low temperatures, although in many cases yield and tensile strengths increase as the temperature goes down.

Materials selection for low-temperature service is a specialized area. In general, it is necessary to select materials and fabrication methods which will provide adequate toughness at all operating conditions. It is frequently necessary to specify Charpy V-notch (or other appropriate) qualification tests to demonstrate adequate toughness of carbon and low-alloy steels at minimum operating temperatures.

Stainless Steels Chromium-nickel steels are suitable for service at temperatures as low as –250°C (–425°F). Type 304 is the most popular. The original cost of stainless steel may be higher than that of another metal, but ease of fabrication (no heat treatment) and welding, combined with high strength, offsets the higher initial cost. Sensitization or formation of chromium carbides can occur in several stainless steels during welding, and this will affect impact strength. However, tests have shown that impact properties of types 304 and 304L are not greatly affected by sensitization but that the properties of 302 are impaired at –185°C (–300°F).

Nickel Steel Low-carbon 9 percent nickel steel is a ferritic alloy developed for use in cryogenic equipment operating as low as –195°C (–320°F). ASTM specifications A 300 and A 353 cover low-carbon 9 percent nickel steel (A 300 is the basic specification for low-temperature ferritic steels). Refinements in welding and (ASME code-approved) elimination of postweld thermal treatments make 9 percent steel competitive with many low-cost materials used at low temperatures.

Aluminum Aluminum alloys have unusual ability to maintain strength and shock resistance at temperatures as low as –250°C (–425°F). Good corrosion resistance and relatively low cost make these alloys very popular for low-temperature equipment. For most welded construction the 5000-series aluminum alloys are widely used. These are the aluminum-magnesium and aluminum-magnesium-manganese materials.

Copper and Alloys With few exceptions the tensile strength of copper and its alloys increases quite markedly as the temperature goes down. However, copper's low structural strength becomes a problem when constructing large-scale equipment. Therefore, alloy must be used. One of the most successful for low temperatures is silicon bronze, which can be used to –195°C (–320°F) with safety.

HIGH-TEMPERATURE MATERIALS

Metals Successful applications of metals in high-temperature process service depend on an appreciation of certain engineering factors. The important alloys for service up to 1,100°C (2,000°F) are shown in Table 28-35. Among the most important properties are creep, rupture, and short-time strengths (see Figs. 28-23 and 28-24). **Creep** relates initially applied stress to rate of plastic flow. **Stress rupture** is another important consideration at high temperatures since it relates stress and time to produce rupture. As the figures show, ferritic alloys are weaker than austenitic compositions, and in both groups molybdenum increases strength. Austenitic castings are much stronger than their wrought counterparts. And higher strengths are available in the superalloys. Other properties which become important at high temperatures include thermal conductivity, thermal expansion, ductility at temperature, alloy composition, and stability.

Actually, in many cases strength and mechanical properties become of secondary importance in process applications, compared with resistance to the corrosive surroundings. All common heat-resistant alloys form oxides when exposed to **hot oxidizing environments.** Whether the alloy is resistant depends upon whether the oxide is stable and forms a protective film. Thus, mild steel is seldom used above 480°C (900°F) because of excessive scaling rates. Higher temperatures require **chromium** (see Fig. 28-25). Thus, type 502 steel, with 4 to 6 percent Cr, is acceptable to 620°C (1,150°F). A 9 to 12 percent Cr steel will handle 730°C (1,350°F); 14 to 18 percent Cr extends the limit to 800°C (1,500°F); and 27 percent Cr to 1,100°C (2,000°F).

The well-known austenitic stainless steels have excellent oxidation resistance: up to 900°C (1,650°F) for 18-8; and up to 1,100°C (2000°F) for 25-12 (and Inconel 600 and Incoloy 800). The cobalt-

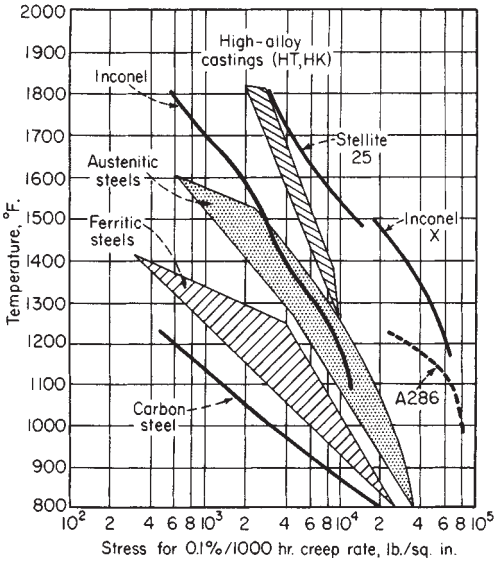


FIG. 28-23 Effect of creep on metals for high-temperature use. °C = (°F – 32) × 5/9; to convert lbf/in² to MPa, multiply by 6.895×10^{-3}. [Chem. Eng., *139* (*Dec. 15, 1958*).]

TABLE 28-22 Typical Property Ranges for Plastics

Thermosets[a]	Specific gravity	Tensile strength		Modulus of elasticity, tension		Impact strength, Izod[b]		Maximum use temperature (no load)		HDT at 254 lbf/in^2[c]		Chemical resistance[d]					
		kip	MPa	10^3kip/in^2	10^3MPa	ft·lb	J	°F	°C	°F	°C	Weather resistance	Weak acid	Strong acid	Weak alkali	Strong alkali	Solvents
Alkyds																	
Glass-filled	2.12–2.15	4–9.5	28–66	20–28	138–193	0.6–10	0.8–14	450	230	400–500	200–260	R	A	A	A	A	A
Mineral-filled	1.60–2.30	3–9	21–62	5–30	34–207	0.3–0.5	0.4–0.7	300–450	150–230	350–500	180–260	R	R	A	A	D	A
Asbestos-filled	1.65	4.5–7	31–48			0.4–0.5	0.6–0.7	450	230	315	160	R	R	S	R	S	R
Synthetic fiber-filled	1.24–2.10	4.5–7	31–48	20	138	0.5–4.5	0.7–6.1	300–430	150–220	245–430	120–220	R	R	S	R	S	A
Alkyl diglycol carbonate	1.30–1.40	5–6	34–41	3.0	21	0.2–0.4	0.3–0.5	212	100	140–190	60–90	R	R	A[e]	R	R-S	R
Diallyl phthalates																	
Glass-filled	1.61–1.78	6–11	41–76	14–22	97–152	0.4–15	0.5–20	300–400	150–200	330–540	165–280	R	R	S	R-S	S	R
Mineral-filled	1.65–1.68	5–9	34–62	12–22	83–152	0.3–0.5	0.4–1	300–400	150–200	320–540	160–280	R	R	S	R-S	S	R
Asbestos-filled	1.55–1.65	7–8	48–55	12–22	83–152	0.4–0.5	0.5–0.7	300–400	150–200	320–540	160–280	R	R	S	R-S	S	R
Epoxies (*bis*-A)																	
No filler	1.06–1.40	4–13	28–90	2.15–5.2	15–36	0.2–1.0	0.3–1.4	250–500	120–260	115–500	45–260	R	R	A	R	S	R-S
Graphite-fiber reinforced	1.37–1.38	185–200	1280–1380	118–120	814–827							S	R	R	R	R	R-S
Mineral-filled	1.6–2.0	5–15	34–103			0.3–0.4	0.4–0.5	300–500	150–260	250–500	120–260	S	R	R	R	R	R-S
Glass-filled	1.7–2.0	10–30	69–207	30	207	10–30	14–41	300–500	150–260	250–500	120–260	S	R	R-S	R	R	R-S
Epoxies (novolac): no filler	1.12–1.24	5–11	34–76	2.15–5.2	15–36	0.3–0.7	0.4–0.9	400–500	200–260	450–500	230–260	R	R	R	R	R	R
Epoxies (cycloaliphatic): no filler	1.12–1.18	10–17.5	69–121	5–7	34–48			480–550	250–290	500–550	260–290	R	R	R-A	R	R-A	R
Melamines																	
Cellulose-filled	1.45–1.52	5–9	34–62	11	76	0.2–0.4	0.3–0.5	250	120	270	130	S	R-S	D	R	D	R
Flock-filled	1.50–1.55	7–9	48–62			0.4–0.5	0.5–0.7	250	120	270	130	S	R-S	D	R	D	R-S
Asbestos-filled	1.70–2.0	5–7	34–48	20	138	0.3–0.4	0.4–0.5	250–400	120–200	265	130	S	R-S	D	S	S	R
Fabric-filled	1.5	8–11	55–76	14–16	97–110	0.6–1.0	0.8–1.4	250	120	310	150	S	R	D	R	A	R-S
Glass-filled	1.8–2.0	5–10	34–69	24	165	0.6–18	0.8–24	300–400	150–200	400	200	S	R	D	R	R-S	R
Phenolics																	
Wood-flour-filled	1.34–1.45	5–9	34–62	8–17	55–117	0.2–0.6	0.3–0.8	300–350	150–180	300–370	150–190	S	R-S	S-D	S-D	A	R-S
Asbestos-filled	1.45–2.00	4.5–7.5	31–52	10–30	69–207	0.2–0.4	0.3–0.5	350–500	180–260	300–500	150–260	S	R-S	S-D	S-D	A	R-S
Mica-filled	1.65–1.92	5.5–7	38–48	25–50	172–345	0.3–0.4	0.4–0.5	250–300	120–150	300–350	150–180	S	R-S	S-D	S-D	A	R-S
Glass-filled	1.69–1.95	5–18	34–124	19–33	131–228	0.3–18	0.4–24	350–550	180–290	300–600	150–320	S	R-S	S-D	S-D	A	R-S
Fabric-filled	1.36–1.43	3–9	21–62	9–14	62–97	0.8–8	1.1–11	220–250	100–120	250–330	120–170	S	R-S	S-D	S-D	A	R-S
Polybutadienes																	
Very high vinyl (no filler)	1.00	8	55	2	14	1.1	1.5	500	260			S	R	R	R	R	R
Polyesters																	
Glass-filled BMC	1.7–2.3	4–10	28–69	16–25	110–172	1.5–16	2.0–22	300–350	150–180	400–450	200–230	R-E	R-A	S-A	S-A	S-D	A-D
Glass-filled SMC	1.7–2.1	8–20	55–138	16–25	110–172	8–22	11–30	300–350	150–180	400–450	200–230	R-E	R-A	S-A	S-A	S-D	A-D
Glass-cloth reinforced	1.3–2.1	25–50	172–345	19–45	131–310	5–30	7–41	300–350	150–180	400–450	200–230	R-E	R-A	S-A	S-A	S-D	A-D
Silicones																	
Glass-filled	1.7–2.0	4–6.5	28–45	10–15	69–103	3–15	4–20	600	320	600	320	R-S	R-S	R-S	S	S-A	R-A
Mineral-filled	1.8–2.8	4–6	28–41	13–18	90–124	0.3–0.4	0.4–0.5	600	320	600	320	R-S	R-S	R-S	S	S-A	R-A
Ureas																	
Cellulose-filled	1.47–1.52	5.5–13	38–90	10–15	69–103	0.2–0.4	0.3–0.5	170	80	260–290	130–140	S	R-S	A-D	S-A	D	R-S
Urethanes																	
No filler	1.1–1.5	0.2–10	1–69	1–10	7–69	5–NB	7	129–250	90–120			R-S	S	A	S	S-A	R-S

TABLE 28-22 Typical Property Ranges for Plastics (*Concluded*)

Thermosets[a]	Specific gravity	Tensile strength		Modulus of elasticity, tension		Impact strength, Izod[b]		Maximum use temperature (no load)		HDT at 66 lbf/in²[c]		HDT at 264 lbf/in²[c]		Chemical resistance[d]					
		kip/in²	MPa	10^3kip/in²	10^2MPa	ft·lb	J	°F	°C	°F	°C	°F	°C	Weather resistance	Weak acid	Strong acid	Weak alkali	Strong alkali	Solvents
ABS																			
GP	1.05–1.07	5.9	41	3.1	21	6	8	160–200	70–90	210–225	100–110	190–206	90–95	R-E	R	A[e]	R	R	A/R
High-impact	1.01–1.06	4.8	33	2.4	17	7.5	10	140–210	60–100	210–225	100–110	188–211	85–100	R-E	R	A[f]	R	R	A/R
Heat-resistant	1.06–1.08	7.4	51	3.9	27	2.2	3.0	190–230	90–110	225–252	110–120	226–240	110–115	R-E	R	A[f]	R	R	A/R
Trans.	1.07	5.6	39	2.9	20	5.3	7.1	130	55	180	80	165	75	R-E	R	A[f]	R	R	A/R
	1.20	6.0	41	3.2	22	2.5	3.4	130–180	55–80	210–220	100–105	195	90	R-E	R	A[e]	R	R	A/R
Acetals																			
Homopolymers	1.42	10	69	5.2	36	1.4	1.9	195	90	338	170	255	125	R	R	A	R	A-D	R
Copolymers	1.41	8.8	61	4.1	28	1.2–1.6	1.6–2.2	212	100	316	160	230	110	R	R	A	R	R	R
Acrylics																			
GP	1.11–1.19	5.6–11.0	39–76	2.25–4.65	16–32	0.3–2.3	0.4–3.1	130–230	55–110	175–225	80–110	165–210	75–100	R	R	A[e]	R	A	A/R
High-impact	1.12–1.16	5.8–8.0	40–55	2.3–3.3	16–23	0.8–2.3	1.1–3.1	140–195	60–90	180–205	80–95	165–190	75–90	R	R	A[e]	R	R	A/R
	1.21–1.28	8.0–12.5	55–86	3.5–4.8	24–33	0.3–0.4	0.4–0.5	125–200	50–90	170–200	75–95	155–205	70–95	R	R	A[e]	R	A	A/R
Cast	1.18–1.28	9.0–12.5	62–86	3.7–5.0	26–34	0.4–1.5	0.5–2.0	140–200	60–90	165–235	75–115	160–215	70–100	R	R	A[e]	R	A	A/R
Multipolymer	1.09–1.14	6–8	41–55	3.1–4.3	21–30	1–3	1–4	165–175	75–80			185–195	85–90	E	R	A[e]	H	S	A[f]
Cellulosics																			
Acetate	1.23–1.34	3.0–8.0	21–55	1.05–2.55	7–18	1.1–6.8	1.5–9	140–220	60–105	120–209	50–100	111–195	45–90	S	S	D	S	D	D-S
Butyrate	1.15–1.22	3.0–6.9	21–48	0.7–1.8	5–12	3.0–10.0	4–14	140–220	60–105	130–227	55–110	113–202	45–95	S	S	D	S	D	D-S
E cellulose	1.10–1.17	3–8	21–55	0.5–3.5	3–24	1.7–7.0	2.3–9.5	115–185	45–85			115–190	45–90	S	S	D	R	S	D
Nitrate	1.35–1.40	7–8	48–55	1.9–2.2	13–15	5–7	7–9	140	60			140–160	60–70	E	S	D	S	D	D
Propionate	1.19–1.22	4.0–6.5	28–45	1.1–1.8	8–12	1.7–9.4	2.3–13	155–220	70–105	147–250	65–120	111–228	45–110	S	S	D	S	D	D-S
Chloro polyether																			
Ethylene copolymers	1.4	5.4	37	1.5	10	0.4	0.5	290	140	285	140			R-S	R	A[e]	R	R	R
EEA	0.93	2.0	14	0.05	0.3	NB		190	90					S	R	A[e]	R	R	A-D
EVA	0.94	3.6	25	0.02–0.12	0.14–0.8	NB				140–147	60–65	93	35	S	R	A	R	R	A-D
Fluoropolymers																			
FEP	2.14–2.17	2.5–3.9	17–27	0.5–0.7	3–5	NB		400	208	158	70			R	R	R	R	R	R
PTFE	2.1–2.3	1.4	7–28	0.38–0.65	2.6–4.5	2.5–4.0	3.4–5.4	550	290	250	120			R	R	R	R	R	R
CTFE	2.10–2.15	4.6–5.7	32–39	1.8–2.0	12–14	3.5–3.6	4.7–4.9	350–390	180–200	258	125			R	R	R	R	R	S[g]
PVF_2	1.77	7.2	50	1.7	12	3.8	5.2	300	150	300	150	195	90	S	R	A[h]	R	R	R
ETFE and ECTFE	1.68–	6.5–7.0	45–48	2–2.5	14–17	NB		300	150	220	105	160	70	R	R	R	R	R	
Methylpentene	0.83	3.3–3.6	23–25	1.3–1.9	10–13	0.95–3.8	1.3–5.2	275	135					E	R	A[h]	R	R	A
Nylons																			
6/6	1.13–1.15	9–12	62–83	3.85	27	2.0	27	180–300	80–150	360–470	180–240	150–220	165–105	R	R	A	R	R	R-D[i]
6	1.14	12.5	86			1.2	1.6	180–250	80–170	300–365	150–185	140–155	60–70	R	R	A	R	R	R-A[i]
6/10	1.07	7.1	49	2.8	19	1.6	2.2	180	80	300	150			R	R	A	R	R	R-A[i]

8	1.09	3.9	27			>16	>22							R	R	A	R	R	R-A[i]
12	1.01	6.5–8.5	45–59	1.7–2.1	12–14	1.2–4.2	1.6–5.7	175–260	80–125			120–130	50–55	R	R	A	R	R	R-A[i]
Copolymers	1.08–1.14	7.5–11.0	52–76			1.5–19	2–26	180–250	80–120			130–350	55–180	R	R	A	R	R	R-A[i]
Polyesters																			
PET	1.37	10.4	72			0.8	1.1	175	80	240	115	185	85	R	R	A[e]	R	A	R-A[i]
PBT	1.31	8.0–8.2	55–57	3.6	25	1.2–1.3	1.6–1.8	280	140	310	155	130	55	R	R	R	R	A	R
PTMT	1.31	8.2	57			1.0	1.4	270	130	302	150	122	50	R	R	R	R	A	R
Copolymers	1.2	7.3	50			1.0	1.4					154	70						
Polyaryl ether	1.14	7.5	52	3.2	22	10	14	250	120	320	100	300	150	E	R	R	R	R	A
Polyaryl sulfone	1.36	13	90	3.7	26	2	2.7	500	260			525	275	Darkens	R	R	R	R	R
Polybutylene	0.910	3.8	26	0.26	1.8	NB		225	105	215	100	130	55	E	R	A[e]	R	R	
Polycarbonate	1.2	9	62	3.45	24	12–16	16–22	250	120	270–290	130–145	265–285	130–140	R	R	A[e]	A	A	A
PC-ABS	1.14	8.2	57	3.7	26	10	14	220	105	235	115	220	105	R-E	R	A[e]	R	S	A
Polyethylenes																			
LD	0.91–0.93	0.9–2.5	6–17	0.20–0.27	1.4–1.9	NB		180–212	80–100	100–120	40–50	90–105	30–40	E	R	A[e]	R	R	R
HD	0.95–0.96	2.9–5.4	20–37			0.4–14	0.5–19	175–250	80–120	140–190	60–90	110–130	45–55	E	R	R-A[e]	R	R	R
HMW	0.945	2.5	17	1	7	NB				155–180	70–80	105–180	40–80	E	R	A[e]	R	R	R
Ionomer	0.94–0.95	3.4–4.5	23–31	0.3–0.7	2–5	6-NB	8	160–180	70–80	110	45	100–120	40–50	E	A	A[e]	R	R	R
Phenylene oxide-based materials	1.06–1.10	7.8–9.6	54–66	3.5–3.8	24–26	5.0	68	175–220	80–105	230–280	110–140	212–265	100–130	R	R	R	R	R	R-A
Polyphenylene sulfide	1.34	10	69	4.8	33	0.3	0.4	500	260			278	135	R	R	A[e]	R	R	R
Polyimide	1.43	5–7.5	34–52	5.4	37	5–7	7–9	500	260			680	360		R	R	A	A	R
Polypropylenes																			
GP	0.90–0.91	4.8–5.5	33–38	1.6–2.2	11–15	0.4–2.2	0.5–3.0	225–300	105–150	200–230	95–110	125–140	50–60	E	R	A[e]	R	R	R
High-impact	0.90–0.91	3–5	21–34	1.3	9	1.5–12	2–16	200–250	95–120	160–200	70–95	120–135	50–60	E	R	A[e]	R	R	A
Propylene copolymer	0.91	4	28	1.0–1.7	7–12	1.1	1.5	190–240	90–115	185–230	85–110	115–140	45–60	E	R	A[e]	R	R	R
Polystyrenes																			
GP	1.04–1.07	6.0–7.3	41–50	4.5	31	0.3	0.4	150–170	65–80			180–220	80–105	S	R	A[e]	R	R	D
High-impact	1.04–1.07	2.8–4.6	20–32	2.9 4.0	20–28	0.7–1.0	0.9–1.4	140–175	60–80			175–210	80–100	S	R	A[e]	R	R	D
Polysulfone	1.24	10.2	70	3.6	25	1.2	1.6	300	150	360	180	345	175	S	R	R	R	R	R-A
Polyurethanes	1.11–1.25	4.5–8.4	31–58	0.1–3.5	0.7–24	NB		190	90					R-S	S-D	S-D	S-D	S-D	R
Vinyl, rigid	1.3–1.5	5–8	34–55	3–5	21–34	0.5–20	0.7–27	150–175	65–80	135–180	60–80	130–175	55–80	R	R	R-S	R	R	R-A
Vinyl, flexible	1.2–1.7	1–4	7–28			0.5–20	0.7–27	140–175	60–80					S	R	R-S	R	R	R-A
Rigid CPVC	1.49–1.58	7.5–9.0	52–62	3.6–4.7	25–32	1.0–5.6	1.4–7.6	230	110	215–245	100–120	200–235	95–115	R	R	R	R	R	R
PVC-acrylic	1.30–1.35	5.5–6.5	38–45	2.75–3.35	19–23	15	20			180	80	170	80	R	R	S	R	R	A
PVC-ABS	1.10–1.21	2.6–6.0	18–41	0.8–3.4	6–23	10–15	14–20							S	R	R-S	R	R	R-D
SAN	1.08	10–12	69–83	5.0–5.6	34–39	0.4–0.5	0.5–0.7	140–200	60–95			190–220	90–105	S-E	R	A	R	R	A

[a]All values at room temperature unless otherwise listed.
[b]Notched samples.
[c]Heat-deflection temperature.
[d]Ac = acid, and Al = alkali; R = resistant; A = attached; S = slight effects; E = embrittles; D = decomposes.
[e]By oxidizing acids.
[f]By ketones, esters, and chlorinated and aromatic hydrocarbons.
[g]Halogenated solvents cause swelling.
[h]By fuming sulfuric.
[i]Dissolved by phenols and formic acid.
SOURCE: *Plastics Engineering Handbook*, 4th ed., Van Nostrand Reinhold, New York, 1976. Courtesy of National Association of Corrosion Engineers. To convert MPA to lbf/in^2, multiply by 145.04.

TABLE 28-23 Chemical Resistance of Coatings for Immersion Service (Room Temperatures)

	Asphalt, unmodified	Coal tar		Coal tar—epoxy	Coal tar—urethanes	Epoxy: phenolic-baked	Epoxy: amine-cured	Epoxy ester	Furfuryl alcohol	Phenolics, baked	Polyesters (unsaturated)	Polyvinyl chloracetates	Vinyl ester	Urethanes		Vinylidene chloride	Chlorinated rubber
		Hot-applied	Cold-applied											Air-dried	Baked		
Acids																	
Sulfuric, 10%	R	LR	NR	R	R	R	R	LR	R	R	R	R	R	LR	LR	R	R
Sulfuric, 80%		NR	NR		NR	NR	NR	NR	LR	NR	R	NR	R	NR	LR	LR	R
Hydrochloric, 10%	R	LR	NR	LR	LR	R	R	LR	R	R	R	R	R	LR	LR	R	R
Hydrochloric, 35%	R	NR	NR			NR	NR	NR	R	R	R	LR	R	LR	LR	R	R
Nitric, 10%	NR	LR	NR			LR	NR	NR	NR	NR	R	R	R	LR	LR	R	R
Nitric, 50%	NR	NR	NR			NR	NR	NR	NR	NR	NR	NR		NR	NR	LR	NR
Acetic, 100%		NR	NR	NR	NR	NR	NR	NR	LR	LR	NR	NR	LR	NR	NR	NR	NR
Water																	
Distilled	R	R	R	R	LR	R	R	R	R	R	R	R	R	LR	LR		R
Salt water	R	R	R	R	LR	R	R	R	R	R	R	R	R	LR	LR	R	R
Alkalies																	
Sodium hydroxide, 10%	R	R	LR	R	R	R	R	NR	R	NR	R	R	R	LR	LR	LR	R
Sodium hydroxide, 70%		NR	NR		LR	R	R	NR	LR	NR	NR	LR	R	LR	LR	NR	R
Ammonium hydroxide, 10%	R	R	LR	R	R	R	LR	LR	R	NR	R	R	R	LR	R	NR	R
Sodium carbonate, 5%	R	R	R			R						R	R	R	R	R	R
Gases																	
Chlorine	R	NR	NR	LR	NR	LR	LR	LR	NR	NR	R	LR	R	LR	R	LR	R
Ammonia		LR	LR	NR	NR	LR	LR	R	R	NR	NR	LR	R	LR	R	NR	NR
Hydrogen sulfide		R	R	R		R	R		R	R		LR	R	R	R	R	R
Organics																	
Alcohols	R	LR	LR	NR	NR	R	R	LR	R	R	R	R	R	NR	R	R	LR
Aliphatic hydrocarbons	NR	LR	LR	LR	LR	R	R	R	R	R	R	R	R	R	R	R	LR
Aromatic hydrocarbons	NR	NR	NR	NR	LR	R	R	R	R	R	R	NR	LR	R	R	LR	NR
Ketones	NR	NR	NR	NR	NR	LR	LR	NR	LR	R	NR	NR	NR	NR	R	NR	NR
Ethers	NR	NR	NR			LR	LR	NR	LR	R		NR	NR	R	R	NR	NR
Esters	NR	NR	NR	NR	NR	LR	LR	NR	R	R	LR	NR	LR	NR	R	NR	NR
Chlorinated hydrocarbons	NR	NR	NR	NR	LR	LR	LR	NR	LR	R	NR	LR	LR	LR	R	LR	NR
Maximum temperature (dry conditions), °F	150			200	200	250	250	250	300	250–300		160	350				160
Maximum temperature (wet conditions), °F		120	120	150	150	150	150	150	190	160–250	250	150	210			150	140

NOTE: Chemical resistance data are for coatings only. Thin coatings generally are not suitable for substrates such as carbon steel which are corroded significantly (e.g., >20 mils/year) in the test environment. R = recommended; LR = limited recommendation; NR = no recommendation.

SOURCE: NACE TPC-2, *Coatings and Linings for Immersion Service.* Courtesy of National Association of Corrosion Engineers.

TABLE 28-24 Properties of Coatings for Atmospheric Service

	Physical properties	Water resistance	Acid resistance	Alkali resistance	Solvent resistance	Temperature resistance	Weathering	Recoating
Alkyd								
Short-oil alkyd	Hard	Fair	Fair	Poor	Fair	Good	Fair	Easy
Long-oil alkyd	Flexible	Fair	Poor	Poor	Poor	Good	Good	Easy
Silicone alkyd	Tough	Good	Fair	Poor	Fair	Best of group	Very good	Fair
Vinyl alkyd	Tough	Good	Best of group	Poor	Fair	Fair	Very good	Difficult
Vinyl								
Polyvinyl chloride acetate copolymers	Tough	Very good	Excellent	Excellent	(Aliphatic hydrocarbon, good; aromatic hydrocarbon, poor)	Fair, 150°F	Very good	Easy
Vinyl acrylic copolymers	Tough	Good	Very good	Very good	(Alphatic, good; aromatic, poor)	Fair, 150°F	Excellent	Easy
Chlorinated rubber								
Resin-modified	Hard	Very good	Very good	Very good	(Alphatic, good; aromatic, poor)	Fair	Good	Easy
Alkyd-modified	Tough	Good	Fair	Fair	(Aliphatic, good; aromatic, poor)	Fair	Very good	Easy
Water base								
Polyvinyl acetate	Scrub-resistant	Poor	Poor	Poor	Poor	Fair	Very good	Easy
Acrylic polymers	Scrub-resistant	Poor	Poor	Poor	Poor	Fair	Excellent	Easy
Epoxy	Tough	Good	Good	Good	Good	Good	Fair	Difficult
Epoxy								
Epoxyamine	Hard	Good	Good	Good	Very good	Very good	Fair; chalks	Difficult
Epoxy polyamide	Tough	Very good	Fair	Excellent	Fair	Good	Good; chalks	Difficult
Epoxy coal tar	Hard	Excellent	Good	Good	Poor	Good	Poor	Difficult
Epoxyester	Flexible	Good	Fair	Poor	Fair	Good	Good; chalks	Reasonable
Polyurethane								
Air-drying polyurethane varnish	Very tough	Fair	Fair	Fair	Fair	Good	Yellowing	Requires care
Two-package-reactive polyurethane	Tough; hard	Good	Fair	Fair	Good	Good	Some yellowing and chalking	Difficult
Moisture-reactive polyurethane	Very tough; abrasion-resistant	Fair	Fair	Fair	Good	Good	Fades in light; yellows in shade	Difficult
Nonyellowing polyurethane	Fairly hard to rubbery	Good	Fair	Fair	Good	Good	Very good	Difficult
Inorganic zinc								
Water base (sodium or potassium silicate)	Tough; abrasion-resistant; excellent chemical bond	Good	Poor	Poor	Excellent	Excellent	Excellent; unaffected by weather	Easy
Organic base (ethyl silicate)	Tough; hard; excellent bond	Good	Poor	Poor	Good	Excellent	Excellent	Easy

SOURCE: F. L. LaQue, *Marine Corrosion; Causes and Prevention,* Wiley, New York, 1975, pp. 302–305. Courtesy of National Association of Corrosion Engineers.

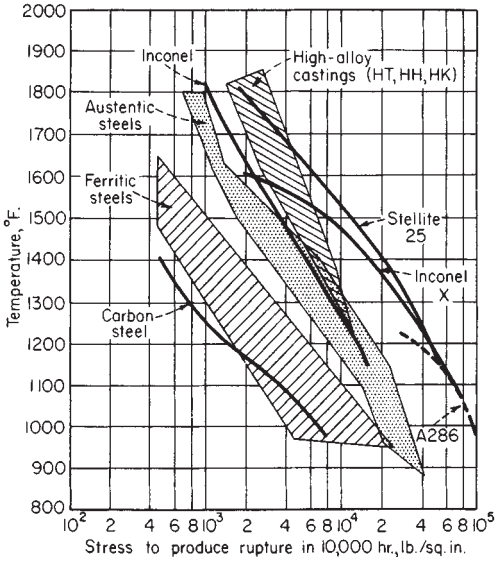


FIG. 28-24 Rupture properties of metals as a function of temperature. °C = (°F − 32) × 5/9; to convert lbf/in² to MPa, multiply by 6.895×10^{-3}. [Chem. Eng., *139 (Dec. 15, 1958).*]

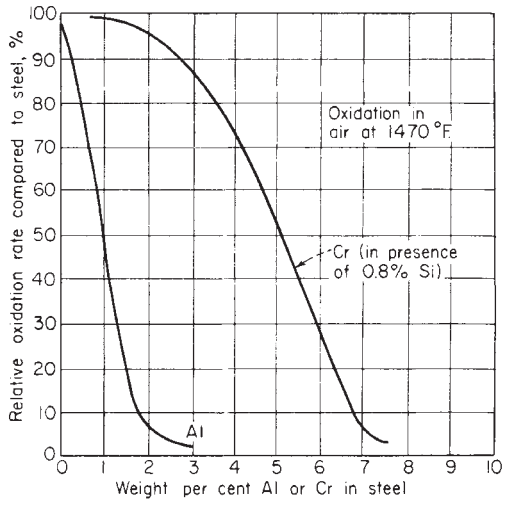


FIG. 28-25 How chromium and aluminum reduce steel oxidation. °C = (°F − 32) × 5/9.

based alloys, of which Stellite 25 is an example, show excellent strengths up to 1,100°C (2,000°F).

Another useful element in imparting oxidation resistance to steel is **silicon** (complementing the effects of chromium). In the lower-chromium ranges, silicon in the amounts of 0.75 to 2 percent is more effective than chromium on a weight-percentage basis. The influence of 1 percent silicon in improving the oxidation rate of steels with varying chromium contents is shown in Fig. 28-26.

Aluminum also improves the resistance of iron to oxidation as well as sulfidation. But use as an alloying agent is limited because the amount required interferes with the workability and high-temperature strength properties of the steel. However, development of high-aluminum surface layers by spraying, dipping, and cementation is a feasible means of improving the heat resistance of low-alloy steels.

Hydrogen Atmospheres Austenitic stainless steels, by virtue of their high chromium contents, are usually resistant to hydrogen atmospheres.

Sulfur Corrosion Chromium is the most important material in imparting resistance to sulfidation (formation of sulfidic scales similar to oxide scales). The austenitic alloys are generally used because of their superior mechanical properties and fabrication qualities, despite the fact that nickel in the alloy tends to lessen resistance to sulfidation somewhat.

Halogens (Hot, Dry Cl_2, HCl) Pure nickel and nickel alloys are useful with dry halogen gases. But even with the best materials, cor-

TABLE 28-25 Typical Physical Properties of Surface Coatings for Concrete

		Polyester		Epoxy		
	Concrete	Isophthalic	Bisphenol	Polyamide	Amine	Urethane*
Tensile strength (ASTM C307), lbf/in²	200–400	1200–2500	1200–2500	600–4000	1200–2500	200–1200
MPa	1.4–2.8	8.3–17	8.3–17	4.0–28	8.3–17	1.4–8.3
Thermal coefficient of expansion (ASTM C531)						
Maximum in/(in·°F)	6.5×10^6	20×10^6	20×10^6	40×10^6	40×10^6	†
Maximum mm/(mm·°C)	11.7×10^6	36×10^6	36×10^6	72×10^6	72×10^6	
Compressive strength, (ASTM) C579), lbf/in²	3500	10,000	10,000	4000	6000	†
MPa	24	70	70	28	42	
Abrasion resistance, Taber abraser—weight loss, mg, 1000-g load/1000 cycles		15–27	15–27	15–27	15–27	†
Shrinkage, ASTM C531, %		2–4	2–4	0.25–0.75	0.25–0.75	0–2
Work life, min		15–45	15–45	30–90	30–90	15–60
Traffic limitations, h after application	Light	16	16	24	24	24
	Heavy	36	36	48	48	48
	Ready for service	48	48	72	72	72
Adhesion characteristics‡		Poor	Fair	Excellent	Good	Fair
Flexural strength (ASTM C580), lbf/in²		1500	1500	1000	1500	†
MPa		10	10	7	10	

NOTE: All physical values depend greatly on reinforcing. Values are for ambient temperatures.

*Type of urethane used is one of three: (1) Type II, moisture-cured; (2) Type IV, two-package catalyst; or (3) Type V, two-package polyol. (Ref. ASTM C16.)

†Urethanes not shown because of great differences in physical properties, depending on formulations. Adhesion characteristics should be related by actual test data. Any system which shows concrete failure when tested for surfacing adhesion should be rated excellent with decreasing rating for systems showing failure in cohesion or adhesion below concrete failure.

‡Adhesion to concrete: primers generally are used under polyesters and urethanes to improve adhesion.

SOURCE: NACE RP-03-76, *Monolithic Organic Corrosion Resistant Floor Surfacing*, 1976. Courtesy of National Association of Corrosion Engineers.

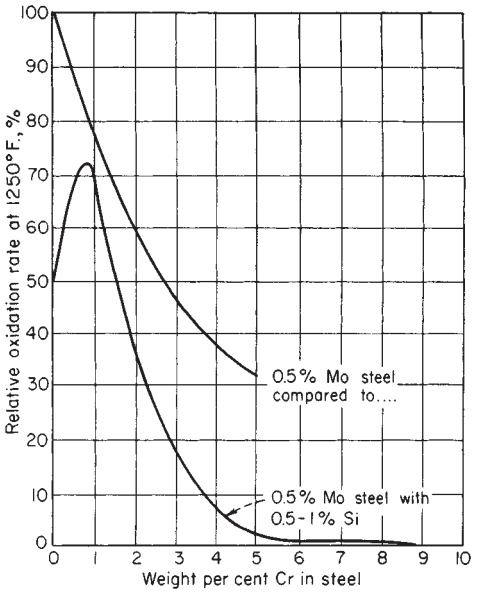


FIG. 28-26 Effect of silicon on oxidation resistance. °C = (°F − 32) × 5/9.

rosion rates are relatively high at high temperature. There are cases in which equipment for high-temperature halogenation has used platinum-clad nickel-base alloys. These materials have high initial cost but long life. Platinum and gold have excellent resistance to dry HCl even at 1,100°C (2,000°F).

Refractories Refractories are selected to accomplish four objectives:

1. Resist heat
2. Resist high-temperature chemical attack
3. Resist erosion by gas with fine particles
4. Resist abrasion by gas with large particles

Refractories are available in three general physical forms: solids in the form of brick and monolithic castable ceramics and as ceramic fibers.

The primary method of selection of the type of refractory to be used is by gas velocity:

<7.5 m/s (25 ft/s): fibers
7.5–60 m/s (25–200 ft/s): monolithic castables
>60 m/s (200 ft/s): brick

Within solids the choice is a trade-off because, with brick, fine particles in the gas remove the mortar joints and, in the monolithic castables, while there are no joints, the refractory is less dense and less wear-resistant.

Internal Insulation The practice of insulating within the vessel (as opposed to applying insulating materials on the equipment exterior) is accomplished by the use of fiber blankets and lightweight aggregates in ceramic cements. Such construction frequently incorporates a thin, high-alloy shroud (with slip joints to allow for thermal expansion) to protect the ceramic from erosion. In many cases this design is more economical than externally insulated equipment because it allows use of less expensive lower-alloy structural materials.

Refractory Brick Nonmetallic refractory materials are widely used in high-temperature applications in which the service permits the appropriate type of construction. The more important classes are described in the following paragraphs.

Fireclays can be divided into plastic clays and hard flint clays; they may also be classified as to alumina content. **Firebricks** are usually made of a blended mixture of flint clays and plastic clays which is formed, after mixing with water, to the required shape. Some or all of the flint clay may be replaced by highly burned or calcined clay, called grog. A large proportion of modern brick production is molded by the dry-press or power-press process, in which the forming is carried out under high pressure and with a low water content. Extruded and hand-molded bricks are still made in large quantities.

The dried bricks are burned in either periodic or tunnel kilns at temperatures ranging between 1,200 and 1,500°C (2,200 and 2,700°F). Tunnel kilns give continuous production and a uniform burning temperature.

Fireclay bricks are used in kilns, malleable-iron furnaces, incinerators, and many portions of metallurgical furnaces. They are resistant to spalling and stand up well under many slag conditions but are not generally suitable for use with high-lime slags or fluid-coal-ash slags or under severe load conditions.

High-alumina bricks are manufactured from raw materials rich in alumina, such as diaspore. They are graded into groups with 50, 60, 70, 80, and 90 percent alumina content. When well fired, these bricks contain a large amount of mullite and less of the glassy phase than is present in firebricks. Corundum is also present in many of these bricks. High-alumina bricks are generally used for unusually severe temperature or load conditions. They are employed extensively in lime kilns and rotary cement kilns, in the ports and regenerators of glass tanks, and for slag resistance in some metallurgical furnaces; their price is higher than that of firebrick.

Silica bricks are manufactured from crushed ganister rock containing about 97 to 98 percent silica. A bond consisting of 2 percent lime is used, and the bricks are fired in periodic kilns at temperatures of 1,500 to 1,540°C (2,700 to 2,800°F) for several days until a stable volume is obtained. They are especially valuable when good strength is required at high temperatures. Superduty silica bricks are finding some use in the steel industry. They have a lowered alumina content and often a lowered porosity.

Silica bricks are used extensively in coke ovens, the roofs and walls of open-hearth furnaces, and the roofs and sidewalls of glass tanks and as linings of acid electric steel furnaces. Although silica brick is readily spalled (cracked by a temperature change) below red heat, it is very stable if the temperature is kept above this range and for this reason

TABLE 28-26 Chemical Resistance of Rubbers

Type of rubber	Features
Butadiene styrene	General-purpose; poor resistance to hydrocarbons, oils, and oxidizing agents
Butyl	General-purpose; relatively impermeable to air; poor resistance to hydrocarbons and oils
Chloroprene	Good resistance to aliphatic solvents; poor resistance to aromatic hydrocarbons and many fuels
Chlorosulfonated polyethylene	Excellent resistance to oxidation, chemicals, and heat; poor resistance to aromatic oils and most fuels
cis-Polybutadiene	General-purpose; poor resistance to hydrocarbons, oils, and oxidizing agents
cis-Polyisoprene	General-purpose; poor resistance to hydrocarbons, oils, and oxidizing agents
Ethylene propylene	Excellent resistance to heat and oxidation
Fluorinated	Excellent resistance to high temperature, oxidizing acids, and oxidation; good resistance to fuels containing up to 30% aromatics
Natural	General-purpose; poor resistance to hydrocarbons, oils, and oxidizing agents
Nitrile (butadiene acrylonitrile)	Excellent resistance to oils, but not resistant to strong oxidizing agents; resistance to oils proportional to acrylonitrile content
Polysulfide	Good resistance to aromatic solvents; unusually high impermeability to gases; poor compression set and poor resistance to oxidizing acids
Silicone	Excellent resistance over unusually wide temperature range [–100 to 260°C (–150 to 500°F)]; fair oil resistance; poor resistance to aromatic oils, fuels, high-pressure steam, and abrasion
Styrene	Synonymous with butadiene-styrene

TABLE 28-27 Properties of Elastomers

Property	NR Natural rubber (*cis*-polyisoprene)	SBR Butadiene styrene (GR-S)	IR Synthetic (polyisoprene)	COX Butadiene acrylonitrile (nitrile)	CR Chloroprene (neoprene)	ITR Butyl (isobutylene isoprene)	BR Polybutadiene	T Polysulfide	Silicone (polysiloxane)
Physical properties									
Specific gravity (ASTM D 792)	0.93	0.91	0.93	0.98	1.25	0.90	0.91	1.35	1.1–1.6
Thermal conductivity, Btu [(h·ft²)(°F/ft)] (ASTM C 177)	0.082	0.143	0.082	0.143	0.112	0.053			0.13
Coefficient of thermal expansion (cubical), 10^{-5}°F (ASTM D 696)	37	37		39	34	32	37.5		45
Electrical insulation	Good	Good	Good	Fair	Fair	Good	Good	Fair	Excellent
Flame resistance	Poor	Poor	Poor	Poor	Good	Poor	Poor	Poor	Good
Minimum, recommended service temperature, °F	–60	–60	–60	–60	–40	–50	–150	–60	–178
Maximum, recommended service temperature, °F	180	180	180	300	240	300	200	250	600
Mechanical properties									
Tensile strength, lbf/in²									
Pure gum (ASTM D 412)	2500–3500	200–300	2500–3500	500–900	3000–4000	2500–3000	200–1000	250–400	600–1300
Black (ASTM D 412)	3500–4500	2500–3500	3500–4500	3000–4500	3000–4000	2500–3000	2000–3000	>1000	
Elongation, %									
Pure gum (ASTM D 412)	750–850	400–600		300–700	800–900	750–950	400–1000	450–650	100–500
Black (ASTM D 412)	550–650	500–600	300–700	300–650	500–600	650–850	450–600	150–450	
Hardness (durometer)	A30–90	A40–90	A40–80	A40–95	A20–95	A40–90	A40–90	A40–85	A30–90
Rebound									
Cold	Excellent	Good	Excellent	Good	Very good	Bad	Excellent	Good	Very good
Hot	Excellent	Good	Excellent	Good	Very good	Very good	Excellent	Good	Very good
Tear resistance	Excellent	Fair	Excellent	Good	Fair to good	Good	Fair	Poor	Fair
Abrasion resistance	Excellent	Good to excellent	Excellent	Good to excellent	Good	Good to excellent	Excellent	Poor	Poor
Chemical resistance									
Sunlight aging	Poor	Poor	Fair	Poor	Very good	Very good	Poor	Very good	Excellent
Oxidation	Good	Good	Excellent	Good	Excellent	Excellent	Good	Very good	Excellent
Heat aging	Good	Very good	Good	Excellent	Excellent	Excellent	Good	Fair	Excellent
Solvents									
Aliphatic hydrocarbons	Poor	Poor	Poor	Excellent	Good	Poor	Poor	Excellent	Fair
Aromatic hydrocarbons	Poor	Poor	Poor	Good	Fair	Poor	Poor	Excellent	Poor
Oxygenated, alcohols	Good	Good	Good	Good	Very good	Very good		Very good	Excellent
Oil, gasoline	Poor	Poor	Poor	Excellent	Good	Poor	Poor	Excellent	Poor
Animal, vegetable oils	Poor to good	Poor to good		Excellent	Excellent	Excellent	Poor to good	Excellent	Excellent
Acids									
Dilute	Fair to good	Fair to good	Fair to good	Good	Excellent	Excellent		Good	Very good
Concentrated	Fair to good	Fair to good	Fair to good	Good	Good	Excellent		Good	Good
Permeability to gases	Low	Low	Low	Very low	Low	Very low	Low	Very low	High
Water-swell resistance	Fair	Excellent	Excellent	Excellent	Fair to excellent	Excellent	Excellent	Excellent	Excellent

stands up well in regenerative furnaces. Any structure of silica brick should be heated up slowly to the working temperature; a large structure often requires 2 weeks or more.

Magnesite bricks are made from crushed magnesium oxide, which is produced by calcining raw magnesite rock to high temperatures. A rock containing several percent of iron oxide is preferable, as this permits the rock to be fired at a lower temperature than if pure materials were used. Magnesite bricks are generally fired at a comparatively high temperature in periodic or tunnel kilns. A large proportion of magnesite brick made in the United States uses raw material extracted from seawater.

Magnesite bricks are basic and are used whenever it is necessary to resist high-lime slags, as in the basic open-hearth steel furnace. They also find use in furnaces for the lead- and copper-refining industries. The highly pressed unburned bricks find extensive use as linings for cement kilns. Magnesite bricks are not so resistant to spalling as fireclay bricks.

Chrome bricks are manufactured in much the same way as magnesite bricks but are made from natural chromite ore. Commercial ores always contain magnesia and alumina. Unburned hydraulically pressed chrome bricks are also available.

Chrome bricks are very resistant to all types of slag. They are used as separators between acid and basic refractories, also in soaking pits and floors of forging furnaces. The unburned hydraulically pressed bricks now find extensive use in the walls of the open-hearth furnace. Chrome bricks are used in sulfite-recovery furnaces and to some extent in the refining of nonferrous metals. Basic bricks combining various properties of magnesite and chromite are now made in large quantities and have advantages over either material alone for some purposes.

The **insulating firebrick** is a class of brick that consists of a highly porous fire clay or kaolin. Such bricks are light in weight (about one-half to one-sixth of the weight of fireclay), low in thermal conductivity, and yet sufficiently resistant to temperature to be used successfully on

TABLE 28-27 Properties of Elastomers (*Concluded*)

Property	ECO, CO Epichlrohydrin homopolymer and copolymer	Fluorosilicone	EPDM Ethylene propylene	CSM Chlorosulfonated polyethylene	FPM Fluorocarbon elastomers
Physical properties					
Specific gravity	1.32–1.49	1.4	0.86	1.1–1.26	1.4–1.95
Thermal conductivity, Btu/[(h·ft²)(°F/ft)]		0.13		0.065	0.13
Coefficient of thermal expansion, 10^{-5}/°F		45		27	8.8
Flame resistance	Fair	Poor	Poor	Good	Excellent
Colorability	Good	Good	Excellent	Excellent	Good
Mechanical properties					
Hardness (Shore A)	30–95	40–70	30–90	45–95	65–90
Tensile strength, kip/in²					
Pure gum		1	<1	4	<2
Reinforced	2–3	<2	0.8–3.2	1.5–2.5	1.5–3
Elongation, % reinforced	320–350	200–400	200–600	250–500	100–450
Resilience	Poor to excellent	Good to fair	Good	Good	Fair
Compression-set resistance	Very good		Good	Fair to good	Good to excellent
Hysteresis resistance	Good	Good	Good	Good	Good
Flexcracking resistance	Very good	Good	Good	Good	Good
Slow rate	Very good	Good	Good	Good	Good
Fast rate	Good	Good	Good	Good	Good
Tear strength	Good	Fair	Poor to fair	Fair to good	Poor to fair
Abrasion resistance	Fair to good	Poor	Good	Excellent	Good
Electrical properties					
Dielectric strength	Fair	Good	Excellent	Excellent	Good
Electrical insulation	Fair	Good	Very good	Good	Fair to good
Thermal properties					
Service temperature, °F					
Minimum, for continuous use	–15 to –80	–90	–60	–40	–10
Maximum, for continuous use	300	400	<350	<325	<500
Corrosion resistance					
Weather	Excellent	Excellent	Excellent	Excellent	Excellent
Oxidation	Very good	Excellent	Excellent	Excellent	Outstanding
Ozone	Good to excellent	Excellent	Excellent	Excellent	Excellent
Radiation		Good	Excellent	Fair to good	Fair to good
Water	Good	Excellent	Good to excellent	Good	Good
Acids	Good	Very good to excellent	Good to excellent	Excellent	Good to excellent
Alkalies	Good	Very good	Good to excellent	Excellent	Poor to good
Aliphatic hydrocarbons	Excellent	Excellent	Poor	Fair	Excellent
Aromatic hydrocarbons	Very good	Excellent	Fair	Poor to fair	Excellent
Halogenated hydrocarbons	Good		Poor	Poor to fair	Good
Alcohol	Good		Good	Very good	Excellent
Synthetic lubricants (diester)	Fair to good	Excellent	Poor to fair	Poor	Fair to good
Hydraulic fluids					
Silicates	Very good	Excellent	Fair to good	Good	Good
Phosphates	Poor to fair	Excellent	Good to excellent	Poor to fair	Poor

SOURCE: C. H. Harper, *Handbook of Plastics and Elastomers,* McGraw-Hill, New York, 1975, Table 35. Courtesy of National Association of Corrosion Engineers. °C = (°F – 32) × 5/9; to convert Btu/(h·ft·°F) to W/(m·°C), multiply by 0.861; to convert lbf/in² to MPa, multiply by 6.895×10^{-3}.

the hot side of the furnace wall, thus permitting thin walls of low thermal conductivity and low heat content. The **low heat content** is particularly valuable in saving fuel and time on heating up, allows rapid changes in temperature to be made, and permits rapid cooling. These bricks are made in a variety of ways, such as mixing organic matter with the clay and later burning it out to form pores; or a bubble structure can be incorporated in the clay-water mixture which is later preserved in the fired brick. The insulating firebricks are classified into several groups according to the maximum use limit; the ranges are up to 870, 1,100, 1,260, 1,430, and above 1,540°C (1,600, 2,000, 2,300, 2,600, and above 2,800°F).

Insulating refractories are used mainly in the heat-treating industry for furnaces of the periodic type. They are also used extensively in stress-relieving furnaces, chemical-process furnaces, oil stills or heaters, and the combustion chambers of domestic-oil-burner furnaces. They usually have a life equal to that of the heavy brick that they replace. They are particularly suitable for constructing experimental or laboratory furnaces because they can be cut or machined readily to any shape. They are not resistant to fluid slag.

There are a number of types of special brick obtainable from individual producers. **High-burned kaolin refractories** are particularly valuable under conditions of severe temperature and heavy load or severe spalling conditions, as in the case of high-temperature oil-fired boiler settings or piers under enameling furnaces. Another brick for the same uses is a high-fired brick of Missouri aluminous clay.

There are on the market a number of bricks made from **electrically fused materials,** such as fused mullite, fused alumina, and fused magnesite. These bricks, although high in cost, are particularly suitable for certain severe conditions.

Bricks of **silicon carbide,** either recrystallized or clay-bonded, have a high thermal conductivity and find use in muffle walls and as a slag-resisting material.

Other types of refractory that find use are forsterite, zirconia, and zircon. Acid-resisting bricks consisting of a dense body like stoneware

TABLE 28-28 Important Properties of Gasket Materials

Material	Maximum service temperature, °F	Important properties
Rubber (straight)		
Natural	225	Good mechanical properties. Impervious to water. Fair to good resistance to acids, alkalies. Poor resistance to oils, gasoline. Poor weathering, aging properties.
Styrene-butadiene (SBR)	250	Better water resistance than natural rubber. Fair to good resistance to acids, alkalies. Unsuitable with gasoline, oils and solvents.
Butyl	300	Very good resistance to water, alkalies, many acids. Poor resistance to oils, gasoline, most solvents (except oxygenated).
Nitrile	300	Very good water resistance. Excellent resistance to oils, gasoline. Fair to good resistance to acids, alkalies.
Polysulfide	150	Excellent resistance to oils, gasoline, aliphatic and aromatic hydrocarbon solvents. Very good water resistance, good alkali resistance, fair acid resistance. Poor mechanical properties.
Neoprene	250	Excellent mechanical properties. Good resistance to nonaromatic petroleum, fatty oils, solvents (except aromatic, chlorinated, or ketone types). Good water and alkali resistance. Fair acid resistance.
Silicone	600	Excellent heat resistance. Fair water resistance; poor resistance to steam at high pressures. Fair to good acid, alkali resistance. Poor (except fluorosilicone rubber) resistance to oils, solvents.
Acrylic	450	Good heat resistance but poor cold resistance. Good resistance to oils, aliphatic and aromatic hydrocarbons. Poor resistance to water, alkalies, some acids.
Chlorosulfonated polyethylene (Hypalon)	250	Excellent resistance to oxidizing chemicals, ozone, weathering. Relatively good resistance to oils, grease. Poor resistance to aromatic or chlorinated hydrocarbons. Good mechanical properties.
Fluoroelastomer (Viton, Fluorel 2141, Kel-F)	450	Can be used at high temperatures with many fuels, lubricants, hydraulic fluids, solvents. highly resistant to ozone, weathering. Good mechanical properties.
Asbestos		
Compressed asbestos-rubber sheet	To 700	Large number of combinations available; properties vary widely depending on materials used.
Asbestos-rubber woven sheet	To 250	Same as above.
Asbestos-rubber (beater addition process)	400	Same as above.
Asbestos composites	To 1000	Same as above.
Asbestos-TFE	500	Combines heat resistance and sealing properties of asbestos with chemical resistance of TFE.
Cork compositions	250	Low cost. Truly compressible materials which permit substantial deflections with negligible side flow. Conform well to irregular surfaces. High resistance to oils; good resistance to water, many chemicals. Should not be used with inorganic acids, alkalies, oxidizing solutions, live steam.
Cork rubber	300	Controlled compressibility properties. Good conformability, fatigue resistance. Chemical resistance depends on kind of rubber used.
Plastics		
TFE (solid) (Tetrafluoroethylene, Teflon)	500	Excellent resistance to almost all chemicals and solvents. Good heat resistance; exceptionally good low-temperature properties. Relatively low compressibility and resilience.
TFE (filled)	To 500	Selectively improved mechanical and physical properties. However, fillers may lower resistance to specific chemicals.
TFE composites	To 500	Chemical and heat resistance comparable with solid TFE. Inner gasket material provides better resiliency and deformability.
CFE (Chlorotrifluoroethylene, Kel-F)	350	Higher cost than TFE. Better chemical resistance than most other gasket materials, although not quite so good as TFE.
Vinyl	212	Good compressibility, resiliency. Resistant to water, oils, gasoline, and many acids and alkalies. Relatively narrow temperature range.
Polyethylene	150	Resists most solvents. Poor heat resistance.
Plant fiber		
Neoprene-impregnated wood fiber	175	Nonporous; recommended for glycol, oil, and gasoline to 175°F.
SBR-bonded cotton	230	Good water resistance.
Nitrile rubber-cellulose fiber		Resists oil at high temperatures.
Vegetable fiber, glue binder	212	Resists oil and water to 212°F.
Vulcanized fiber		Low cost, good mechanical properties. Resists gasoline, oils, greases, waxes, many solvents.
Inorganic fibers	To 2200°F	Excellent heat resistance, poor mechanical properties.
Felt		
Pure felt		Resilient, compressible and strong, but not impermeable. Resists medium-strength mineral acids and dilute mineral solutions if not intermittently dried. Resists oils, greases, waxes, most solvents. Damaged by alkalies.
TFE-impregnated	300	Good chemical and heat resistance.
Petrolatum or paraffin-impregnated		High water repellency.
Rubber-impregnated		Many combinations available; properties vary widely depending on materials used.
Metal		
Lead	500	Good chemical resistance. Best conformability of metal gaskets.
Tin		Good resistance to neutral solutions. Attacked by acids, alkalies.
Aluminum	800	High corrosion resistance. Slightly attacked by strong acids, alkalies.
Copper, brass		Good corrosion resistance at moderate temperatures.
Nickel	1400	High corrosion resistance.
Monel	1500	High corrosion resistance. Good against most acids and alkalies, but attacked by strong hydrochloric and strong oxidizing acids.
Inconel	2000	Excellent heat, oxidation resistance.
Stainless steel		High corrosion resistance. Properties depend on type used.

TABLE 28-28 Important Properties of Gasket Materials (*Concluded*)

Material	Maximum service temperature, °F	Important properties
Metal composites		Many combinations available; properties vary widely depending on materials used.
Leather	220	Low cost. Limited chemical and heat resistance. Not recommended against pressurized steam, acid or alkali solutions.
Glass fabric		High strength and heat resistance. Can be impregnated with TFE for high chemical resistance.
Packing and sealing materials		
Rubber (straight)	To 600	See Gasket Materials for properties. Mainly used for ring-type seals, although some types are available as spiral packings.
Rubber composites:		
Cotton-reinforced	350	High strength. Chemical resistance depends on type of rubber used; however, most types are noted for high resistance to water, aqueous solutions.
Asbestos-reinforced	450	High strength combined with good heat resistance.
Asbestos:		
Plain, braided asbestos	500	Heat resistance combined with resistance to water, brine, oil, many chemicals. Can be reinforced with wire.
Impregnated asbestos	To 750	Environmental properties vary widely depending on type of asbestos and impregnant used. Neoprene-cemented type resists hot oils, gasoline, and solvents. Oil and wax-impregnated type resists caustics. Wax-impregnated blue asbestos type has high acid resistance. TFE-impregnated type has good all-around chemical resistance.
Asbestos composites	To 1200	End properties vary widely depending on secondary material used.
Metals		
Copper	To 1500	Properties depend on other construction materials and form of copper used. Packing made of copper foil over asbestos core resists steam and alkalies to 1000°F. Packing of braided copper tinsel resists water, steam, and gases to 1500°F.
Aluminum	To 1000	Resists hot petroleum derivatives, gases, footstuffs, many organic acids.
Lead	550	Many types are available.
Organic fiber		
Flax	300	Good water resistance.
Jute	300	Good water resistance.
Ramie	300	Good resistance to water, brine, cold oil.
Cotton	300	Good resistance to water, alcohol, dilute aqueous solutions.
Rayon	300	Good resistance to water, dilute aqueous solutions.
Felt	300	See Gasket Materials.
Leather	To 210	Good mechanical properties for sealing. Resistant to alcohol, gasoline, many oils and solvents, synthetic hydraulic fluids, water.
TFE	To 500	Available in many forms, all of which have high chemical resistance.
Carbon-graphite	700	Good bearing and self-lubricating properties. Good resistance to chemicals, heat.

TABLE 28-29 Properties of Graphite and Silicon Carbide

	Graphite	Impervious graphite	Impervious silicon carbide
Specific gravity	1.4–1.8	1.75	3.10
Tensile strength, lbf/in^2 (MPa)	400–1400 (3–10)	2,600 (18)	20,650 (143)
Compressive strength, lbf/in^2 (MPa)	2000–6000 (14–42)	10,500 (72)	150,000 (1000)
Flexural strength, lbf/in^2 (MPa)	750–3000 (5–21)	4,700 (32)	
Modulus of elasticity ($\times 10^5$), lbf/in^2 (MPa)	0.5–1.8 ($0.3–12 \times 10^4$)	2.3 (1.6×10^4)	56 (39×10^4)
Thermal expansion, in/(in·°F $\times 10^{-6}$) [mm/(mm·°C)]	0.7–2.1 (1.3–3.8)	2.5 (4.5)	1.80 (3.4)
Thermal conductivity, Btu/[(h·ft^2)(°F/ft)] [(W/(m·K)]	15–97 (85–350)	85 (480)	60 (340)
Maximum working temperature (inert atmosphere), °F (°C)	5000 (2800)	350 (180)	4,200 (2300)
Maximum working temperature (oxidizing atmosphere), °F (°C)	660 (350)	350 (180)	3,000 (1650)

SOURCE: Carborundom Co. Courtesy of National Association of Corrosion Engineers.

TABLE 28-30 Properties of Stoneware and Porcelain

	Stoneware	Porcelain
Specific gravity	2.2–2.7	2.4–2.9
Hardness, Mohs scale	6.5	7.5
Modulus of rupture, lb/in^2	3–7,000	8–15,000
Modulus of elasticity, lb/in^2	$5–10 \times 10^6$	$10–15 \times 10^6$
Compressive strength, lb/in^2	40–60,000	60–90,000
Pore volume, %	1.5	0.2–0.5
Water absorption, %	0.5–4.0	0–0.5
Linear thermal expansion, per °F	2.4×10^{-6}	2.5×10^{-6}
Thermal conductivity, Btu/(ft^2·h·°F·in^{-1})	8–22	8–10

are used for lining tanks and conduits in the chemical industry. Carbon blocks are used as linings for the crucibles of blast furnaces, very extensively in a number of countries and to a limited extent in the United States. Fusion-cast bricks of mullite or alumina are largely used to line glass tanks.

Ceramic-Fiber Insulating Linings Ceramic fibers are produced by melting the same alumina-silica china (kaolin) clay used in conventional insulating firebrick and blowing air to form glass fibers. The fibers, 50.8 to 101.6 mm (2 to 4 in) long by 3 μm in diameter, are interlaced into a mat blanket with no binders or chopped into shorter fibers and vacuum-formed into blocks, boards, and other shapes. Ceramic-fiber linings, available for the temperature range of 650 to 1,430°C (1,200 to 2,600°F), are more economical than brick in the 650- to 1,230°C- (1,200- to 2,250°F-) range. Savings come from reduced first costs, lower installation labor, 90 to 95 percent less weight, and a 25 percent reduction in fuel consumption.

Because of the larger surface area (compared with solid-ceramic refractories) the chemical resistance of fibers is relatively poor. Their acid resistance is good, but they have less alkali resistance than solid materials because of the absence of resistant aggregates. Also, because they have less bulk, fibers have lower gas-velocity resistance. Besides the advantage of lower weight, since they will not hold heat, fibers are more quickly cooled and present no thermal-shock structural problem.

TABLE 28-32 Comparison of Properties of Refractory Metals

Melting point, °F	Element	Advantages	Disadvantages
6180	Tungsten	Highest melting point; nonvolatile oxide to at least 2500°F	Highest density; oxidizing rapidly; brittle at low temperatures
5425	Tantalum	Very high melting point; nonvolatile oxide; ductile	High density; oxidizing rapidly; least abundant
4730	Molybdenum	High melting point; less dense than tungsten or tantalum; moderately ductile at room temperature	Extremely high oxidation rate (volatile oxide)
4380	Niobium (columbium)	High melting point; nonvolatile oxide; ductile; moderate density	Oxidizing rapidly
3435	Chromium	Extremely oxidation-resistant; lightest of refractory metals	Lowest melting point of refractory metals, brittle at low temperatures

Castable Monolithic Refractories Standard portland cement is made of calcium hydroxide. In exposures above 427°C (800°F) the hydroxyl ion is removed from portland (water removed); below 427°C (800°F), water is added. This cyclic exposure results in spalling. Castables are made of calcium aluminate (rather than portland); without the hydroxide they are not subject to that cyclic spalling failure.

Castable refractories are of three types:

1. *Standard.* 40 percent alumina for most applications at moderate temperatures.

TABLE 28-31 Wood for Chemical Equipment

Condition of woods after 31 d immersion in cold solutions
Examined after 7 d drying

	Fir	Oak	Oregon pine	Yellow pine	Spruce	Redwood	Maple	Cypress
Hydrochloric acid, 5%	NAC	NAC	NAC	SS	SS	SS	NAC	NAC
Hydrochloric acid, 10%	NAC	NAC	NAC	SS	SS	SS	NAC	NAC
Hydrochloric acid, 50%	SS,SB,SWF	SS,WF	S,WF	S,WF	S,WF	S,WF	S,WF	S,WF
Sulfuric acid, 1%	NAC	NAC	NAC	SS	SS	NAC	NAC	SS,SB
Sulfuric acid, 5%	SS	SS	SS	SS	SS,SB	SS,SB	NAC	SS,SB
Sulfuric acid, 10%	S,FSD	S,FSD	S,FSD	S,FSD	S,FSD	S,FSD	S,FSD	S,FSD
Sulfuric acid, 25%	SSp,FSD	SSp,FSD	SSp,FSD	SSp,FSD	SSp,FSD	SSp,FSD	SSp,FSD	SSp,FSD
Caustic soda, 5%	S,NAC	MSh,SWp	SS	SS,FSD	SSp,FSD	SSp,FSD	MSh	SSp,FSD
Caustic soda, 10%	S,FSD	MSh,WF,Horny	SS	SS,SB,FSD	SS,SB,FSD	SS,SB,FSD	MSh	S,SB,FSD
Alum, 13%	NAC	NAC	NAC	NAC	NAC	NAC	NAC	NAC
Sodium carbonate, 10%	SB,GC	NAC	GC	SB,GC	SB,GC	SB,GC	GC	SB,GC
Calcium chloride, 25%	NAC	NAC	NAC	NAC	NAC	NAC	NAC	NAC
Common salt, 25%	NAC	NAC	NAC	SS,GC	SS,GC	SS,GC	NAC	NAC
Water	NAC	NAC	NAC	NAC	NAC	NAC	NAC	NAC
Sodium sulfide	SS,SB	MSh,WF	SB	SB	SB	SB	MSh,FSD	FSD

Condition of woods after 8 h boiling in solutions
Examined after 7 d drying

	Fir	Oak	Oregon pine	Yellow pine	Spruce	Redwood	Maple	Cypress
Hydrochloric acid, 10%	SB,S	FSD	FSD	FSD	FSD	FSD	FSD	FSD
Hydrochloric acid, 50%	FD,Ch,B,S,NG	FD,Ch,B,S,NG	FD,Ch,B,S,NG	FD,Ch,B,S,NG	FD,Ch,B,S,NG	FD,Ch,B,S,NG	FD,Ch,B,S,NG	FD,Ch,B,S,NG
Sulfuric acid, 4%	SB,GC	SB,GC	SB,GC	SB,GC	SB,GC	SB,GC	SB,GC	SB,GC
Sulfuric acid, 5%	SS,GC	SB,GC	SB,GC	SB,GC	SB,FSD	SB,GC	SB,GC	SB,FSD
Sulfuric acid, 10%	SS,GC	BFD,Wpd,NG	Sp,FD,NG	B,Sp,FD,NG	B,Sp,FD,NG	SB,FSD	SB,FSD	B,FD
Caustic soda, 5%	SS	MSh	S	GC	S,GC	S,GC	Sh	SSp
Alum, 13%	SB,GC	NAC	NAC	SB,GC	SB,GC	SB,GC	NAC	SB,GC
Sodium carbonate, 10%	SB,GC	GC	GC	GC	GC	GC	GC	SB,GC
Calcium chloride, 25%	SB,GC	SB,SS,GC	NAC	SB,GC	SB,GC	NAC	NAC	SB,GC
Common salt, 25%	NAC	NAC	NAC	SB,GC	NAC	SB,GC	NAC	NAC
Water	NAC	NAC	NAC	SB,GC	NAC	NAC	NAC	NAC

TABLE 28-33 General Physical and Chemical Characteristics of Refractory Brick*

Type of brick	Typical composition	Approx. bulk density, lb/ft³	Fusion point, °F.	Chemical nature	Deformation under hot loading	Apparent porosity, %	Permeability	Hot strength	Thermal shock resistance	Chemical resistance	
										To acid	To alkali
Silica	SiO_2, 95%	115	3100	Acid	Excellent	21	High	Excellent	Poor‡	Good	Good at low temperatures
High-duty fire clay	SiO_2, 54% Al_2O_3, 40%	134	3125	Acid	Fair	18	Moderate	Fair	Fair	Good	Good at low temperatures
Superduty fire clay	SiO_2, 52% Al_2O_3, 42%	140	3170	Acid	Good	15	High	Fair	Good	Good	Good at low temperatures
Acid-resistant (type H)	SiO_2, 59% Al_2O_3, 34%	142	3040	Acid	Poor	7	Low	Poor	Good	Insoluble in acids except HF and boiling phosphoric	Very resistant in moderate concentrations
Insulating brick	Varies	30–75	Varies		Poor	65–85	High	Poor	Excellent	Poor	Poor
High-alumina	Al_2O_3, 50–85%	170	3200–3400	Slightly acid	Good	20	Low	Good	Good	Good except for HF and aqua regia	Very slight attack with hot solutions
Extra-high-alumina	Al_2O_3, 90–99%	185	3000–3650	Neutral	Excellent	23	Low	Excellent	Good		
Mullite	Al_2O_3, 71%	153	3290	Slightly acid	Excellent	20	Low	Good	Good	Insoluble in most acids	Slight reaction
Chrome-fired	Chrome ore, 100%	195	Varies	Neutral	Fair	20	Low	Good	Poor	Fair to good	Poor
Magnesite-chrome bonded§	MgO, 50–80%	190			Good	12	Very low	Good	Excellent		
Magnesite-chrome fired	Cr_2O_3, 5–18% Fe_2O_3, 3–13% Al_2O_3, 6–11%	180	Varies	Basic	Excellent	20	High	Good	Excellent	Fair except to strong acids	Fair resistance at low temperatures
Magnesite-chrome high-fired	SiO_2, 1.2–5%	180			Excellent	18	High	Excellent	Excellent		
Magnesite-bonded§	MgO, 95%	181	3900	Basic	Good	11	Low	Good	Good	Soluble in most acids	Good resistance at low temperatures
Magnesite-fired		178			Good	19	Moderate	Good	Good		
Zircon	ZrO_2, 67% SiO_2, 33%	200	3100†	Acid	Excellent	25	Very low	Excellent	Good	Very slight	Very slight
Zirconia (stabilized)	ZrO_2, 94% CaO, 4%	245	4800	Slightly acid	Excellent	23	Low	Excellent	Excellent	Very slight	Very slight
Silicon-carbide	SiC, 80–90%	160	4175	Slightly acid	Excellent	15	Very low	Excellent	Excellent	Slight reaction with HF	Attacked at high temperatures
Graphite	C, 97%	105	6400	Neutral	Excellent	16	Low	Excellent	Excellent	Insoluble	Insoluble

*From *Chem. Eng.,* 100 (July 31, 1967). To convert lbm/ft³ to kg/m³, multiply by 0.0624; °C = (°F − 32) × 5/9.
†Dissociates above 1700°C (3100°F).
‡Good above 650°C (1200°F).
§Chemically bonded.

TABLE 28-34 Minimum Temperature without Excessive Scaling in Air (Continuous Service)*

Alloy	°F	°C
Carbon steel	1050	565
½Mo steel	1050	565
1Cr ½Mo steel	1100	595
2¼Cr 1Mo steel	1150	620
5Cr ½Mo steel	1200	650
9Cr 1Mo steel	1300	705
AISI 410	1300	705
AISI 304	1600	870
AISI 321	1600	870
AISI 347	1600	870
AISI 316	1600	870
AISI 309	2000	1090
AISI 310	2100	1150

*Courtesy of National Association of Corrosion Engineers.

2. *Intermediate purity.* 50 to 55 percent alumina. The anorthite (needle-structure) form is more resistant to the action of steam exposure.

3. *Very pure.* 70 to 80 percent alumina for high temperatures. Under reducing conditions the iron in the ceramic is controlling, as it acts as a catalyst and converts the CO to CO_2 plus carbon, which results in spalling. The choice among the three types of castables is generally made by economic considerations and the temperature of the application.

Compared with brick, castables are less dense, but this does not really mean that they are less serviceable, as their cements can hydrate and form gels which can fill the voids in castables. Extra-large voids do indicate less strength regardless of filled voids and dictate a lower allowable gas velocity. If of the same density as a given brick, a castable will result in less permeation.

Normally, castables are 25 percent cements and 75 percent aggregates. The aggregate is the more chemically resistant of the two components. The highest-strength materials have 30 percent cement, but too much cement results in too much shrinkage. The standard insulating refractory, 1:2:4 LHV castable, consists of 1 volume of cement, 2 volumes of expanded clay (Haydite), and 4 volumes of vermiculite.

Castables can be modified by a clay addition to keep the mass intact, thus allowing application by air-pressure gunning (gunite). Depending upon the size and geometry of the equipment, many castable linings must be reinforced; wire and expanded metal are commonly used.

TABLE 28-35 Important Commercial Alloys for High-Temperature Process Service

	Nominal composition, %			
	Cr	Ni	Fe	Other
Ferritic steels				
Carbon steel			Bal.	
2¼ chrome	2¼		Bal.	Mo
Type 502	5		Bal.	Mo
Type 410	12		Bal.	
Type 430	16		Bal.	
Type 446	27		Bal.	
Austenitic steels				
Type 304	18	8	Bal.	
Type 321	18	10	Bal.	Ti
Type 347	18	11	Bal.	Cb
Type 316	18	12	Bal.	Mo
Type 309	24	12	Bal.	
Type 310	25	20	Bal.	
Type 330	15	35	Bal.	
Nickel-base alloys				
Nickel		Bal.		
Incoloy 800	21	32	Bal.	
Hastelloy B		Bal.	6	Mo
Hastelloy C	16	Bal.	6	W, Mo
60-15	15	Bal.	25	
Inconel 600	15	Bal.	7	
80-20	20	Bal.		
Hastelloy X	22	Bal.	19	Co, Mo
Multimet	21	20	Bal.	Co
Rene 41	19	Bal.	5	Co, Mo, Ti
Cast irons				
Ductile iron			Bal.	C, Si, Mg
Ni-Resist, D-2	2	20	Bal.	Si, C
Ni-Resist, D-4	5	30	Bal.	Si, C
Cast stainless (ACI types)				
HC	28	4	Bal.	
HF	21	11	Bal.	
HH	26	12	Bal.	
HK	15	20	Bal.	
HT	15	35	Bal.	
HW	12	Bal.	28	
Superalloys				
Inconel X	15	Bal.	7	Ti, Al, Cb
A 286	15	25	Bal.	Mo, Ti
Stellite 25	20	10	Co-base	W
Stellite 21 (cast)	27.3	2.8	Co-base	Mo
Stellite 31 (cast)	25.2	10.5	Co-base	W

Section 29

Process Machinery Drives

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Nomenclature

Symbol	Definition	SI units	U.S. customary units
C	Constant		
C_1	Velocity of steam flow	m/s	ft/s
c	Clearance	m	ft
d	Bearing diameter	m	ft
E	Applied voltage	V	V
E	Modulus of elasticity	N/m^2	lbf/ft^2
e	Gross pump efficiency	Dimensionless	Dimensionless
e	Base of natural logarithm		
e	Efficiency	Dimensionless	Dimensionless
e_h	Hydraulic efficiency	Dimensionless	Dimensionless
F	Load		
F_f	Friction force	N	lbf
f	Friction coefficient		
f	Frequency	Hz	Hz
G, g	Gravitational constant	m/s^2	ft/s^2
H	Power	W	hp
H_g	Enthalpy change, ideal	J	Btu
H_i	Reversible enthalpy change	J/kg	Btu/lb
H_p	Total head (pump)	m	ft
H_t	Total head (turbine)	m	ft
h	Oil thickness	m	ft
Δh	Enthalpy change per mass	J/kg	Btu/lb
I	Line current	A	A
K_A	Constant		
K_L	Constant		
K_S	Constant		
K_T	Constant		
k	Constant		
Mol. wt.	Molecular weight	kg	lb
N	Force	N	lbf
N_c	Compressor efficiency	Dimensionless	Dimensionless
N_e	Expander efficiency	Dimensionless	Dimensionless
n	Speed	r/s	r/min
n_s	Specific speed (turbine or pump)		
P	Pressure	kPa	lbf/in^2
P	Mean bearing pressure	N/m^2	lbf/ft^2
P	Power	kW	kW

Symbol	Definition	SI units	U.S. customary units
PD	Pitch diameter	m	ft
P_{max}	Contact pressure, maximum	N/m^2	lbf/ft^2
p	Number of poles		
Q	Quantity of heat added	J	Btu
Q_c	Quantity of heat removed	J	Btu
Q_p	Capacity, pump	m^3/h	ft^3/h
Q_t	Capacity, turbine	m^3/h	ft^3/h
R	Operating load	kg	lb
R	Gas constant	J/(mol·K)	Btu/(mol·°R)
R	Armature resistance	Ω	Ω
r	Radius	m	ft
S	Apparent power	kVA	kVA
S_{max}	Stress, maximum	N/m^2	lbf/ft^2
T	Tension	N	lbf
T	Torque	N·m	lbf·ft
T	Temperature	K	°R
T_a	Average temperature	K	°R
T_c	Centrifugal tension	N	lbf
t	Time	s	s
V	Applied voltage	V	V
V	Counterelectromotive force	V	V
V	Velocity	m/s	ft/min
W	Net work to compressor	J	Btu
W_c	Compressor work	J	Btu
W_{theor}	Theoretical work	J	Btu
WK^2	Inertia	$kg·m^2$	$lb·ft^2$
y	Power factor	Dimensionless	Dimensionless
Z	Viscosity	$N·s/m^2$	cP
Z_a	Average compressibility factor	Dimensionless	Dimensionless

Greek symbols

α_r	exit angle		
β	exit angle		
θ	Arc of contact		
φ	Belt density	kg/m^3	lb/in^3
μ	peripheral velocity	m/s	ft/min
ϕ	Magnetic-field flux	Wb	Wb
ω	relative velocity	m/s	ft/min

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ELECTRIC MOTORS AND AUXILIARIES

All electric motors operate on the same basic principle regardless of type or size. When a wire carries electric current in the presence of a magnetic field (at least partially perpendicular to the current), a force on the wire is produced perpendicular to both the current and the magnetic field. In a motor the magnetic field radiates either in toward or outward from the motor axis (shaft) across the air gap, which is the annular space between the rotor and stator. Current-carrying conductors parallel to the axis (shaft) then have a force on them tangent to the rotor circumference. The force on the wire opposes an equal force (or reaction) on the magnetic field. It makes no difference whether the magnetic field is created in the rotor or the stator; the net result is the same: the shaft rotates.

Within these basic principles there are many types of electric motors. Each has its own individual operating characteristics peculiarly suited to specific drive applications. Equations (29-1) through (29-9), presented in Table 29-1, describe the general operating characteristics of alternating-current motors. When several types are suitable, selection is based on initial installed cost and operating costs (including maintenance and consideration of reliability).

ALTERNATING-CURRENT MOTORS, CONSTANT SPEED

The majority of industrial drives are constant speed. Typical applications include:

Pumps
Compressors

TABLE 29-1 Useful Formulas for Alternating-Current Motors

Power output:

$$H = Tn/5250 \qquad (29\text{-}1)$$

$$P = 0.00173VIye \quad \text{(three-phase)} \qquad (29\text{-}2)$$

$$P = 0.001VIye \quad \text{(single-phase)} \qquad (29\text{-}3)$$

Power input:

$$P = 0.00173VIy \quad \text{(three-phase)} \qquad (29\text{-}4)$$

$$P = 0.001VIy \quad \text{(single-phase)} \qquad (29\text{-}5)$$

$$P = 0.746H/e \qquad (29\text{-}6a)$$

$$S = P/y = 0.746H/ye \qquad (29\text{-}6b)$$

Line current and power factor:

$$I = \frac{0.746H\ (\text{output})}{0.00173Vye} \quad \text{(three-phase)} \qquad (29\text{-}7)$$

$$I = \frac{0.746H\ (\text{output})}{0.001Vye} \quad \text{(single-phase)} \qquad (29\text{-}8)$$

$$y = \frac{P\ (\text{input})}{S} \qquad (29\text{-}9)$$

where e = efficiency, decimal
H = power, hp
I = line current, A
n = speed, r/min
P = power, kW
S = apparent power, kVA
T = torque, lbf·ft
V = applied voltage, V
y = power factor, decimal

NOTE: To convert horsepower to watts, multiply by 746; to convert pound-force-feet to newton-meters, multiply by 1.356; and to convert revolutions per minute to radians per second, multiply by 0.1047.

Fans
Conveyors
Crushers and mills

Alternating-Current Squirrel-Cage Induction Motors These motors are by far the most common constant-speed drives. They are relatively simple in design and therefore both low in cost and highly reliable. Representative prices are shown in Fig. 29-1 for various speeds and horsepowers.

The typical three-phase squirrel-cage motor has stator windings which are connected to the power source. The rotor is a cylindrical magnetic structure mounted on the shaft with slots in the surface, parallel (or slightly skewed) to the shaft; either bars are inserted into these slots or molten metal is cast in place and connected by a short-circuiting end ring at both ends of the rotor. The name "squirrel-cage" derives from this rotor-bar construction. In operation, current passing through the stator winding creates a rotating magnetic field which cuts the rotor winding unless the rotor is turning in exact synchronism with the stator field. This cutting action induces a voltage, and hence a current, in the rotor which in turn reacts with the magnetic field to produce torque.

The typical medium-sized squirrel-cage motor is designed to operate at 2 to 3 percent slip (97 to 98 percent of synchronous speed). The synchronous speed is determined by the power-system frequency and the stator-winding configuration. If the stator is wound to produce one north and one south magnetic pole, it is a two-pole motor; there is always an even number of poles (2, 4, 6, 8, etc.). The synchronous speed is

$$n = 120\,f/p \qquad (29\text{-}10)$$

where n = speed, r/min
f = frequency, Hz (cycles/s)
p = number of poles

The actual operating speed will be slightly less by the amount of slip. Slip depends upon motor size and application. Typically, the larger the motor, the less slip; an ordinary 7460-W (10-hp) motor may have 2½ percent slip, whereas motors over 746 kW (1000 hp) may have less than ½ percent. High-slip motors (as much as 13 percent slip) are used for applications with high inertia and requiring high starting torque; typical applications are punch presses and some crushers. Typical speed versus torque curves for various National Electrical Manufacturers Association (NEMA) design motors up to 149.2 kW (200 hp) are shown in Fig. 29-2. Typical characteristics and applications for these motors are given in Table 29-2.

As noted in Fig. 29-1 and Table 29-2 motors of various efficiency ratings may be available for an application. The efficiency of all motors of the same design will not be identical because of normal variations inherent in materials, variations in manufacturing processes, and inaccuracies in the test methods and equipment used to determine the efficiency. To address these variations, two values of efficiency have been identified for polyphase induction motors. Nominal efficiency refers to the average efficiency of a large population of motors of duplicate design. Some of the motors will have efficiency lower than the nominal efficiency value, and some will have higher. Minimum efficiency refers to the lowest level of efficiency that any motor in the population might have as a result of the variations introduced by the materials, manufacturing processes, and testing. The nominal effi-

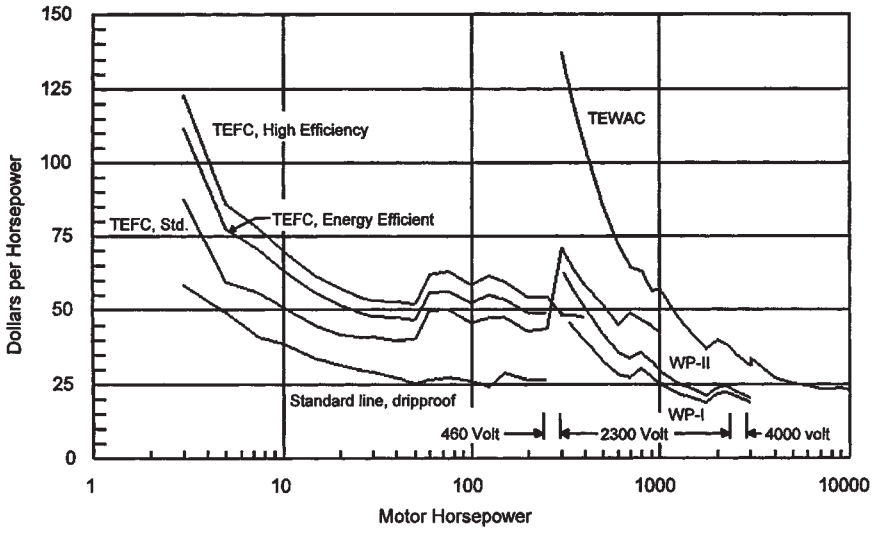


FIG. 29-1 Motor prices in dollars per horsepower for 1800 rev/min squirrel-cage induction motors from 3 to 10,000 hp. Dripproof and TEFC motors shown from 3 to 400 horsepower have 1.15 service factor; for other motors above 250 horsepower, the service factor is 1.0. The basis of these data is July, 1994. To convert dollars per horsepower to dollars per kilowatt, multiply by 1.340; to convert horsepower to kilowatts, multiply by 0.746.

ciency should be used when estimating the power required to supply a number of motors. The NEMA Standard MG-1, *Motors and Generators*, requires that all polyphase squirrel-cage integral horsepower motors, 1 to 500 horsepower, designated as Design A, B (and equivalent Design C ratings), and E be marked with the NEMA nominal efficiency value. A minimum level of efficiency is defined for each level of nominal efficiency in the NEMA Standard MG-1.

A motor purchaser or user can use the defined NEMA nominal efficiency to determine the relative economics of alternate motors. Common to the various methods one can use is consideration of the costs of energy and the motor, the annual hours of operation of the motor, and the motor efficiency. A simple payback analysis is used to determine the number of years required for the savings in energy cost resulting from the use of a more efficient motor to pay back the higher initial cost of the motor. The present worth life-cycle analysis considers both the time value of money and energy cost inflation to determine the present worth of savings for each motor being evaluated. The cash flow and payback analysis method considers motor cost premium, motor depreciation life, energy cost and energy cost inflation rate, corporate tax rate, tax credit, and the motor operating parameters.

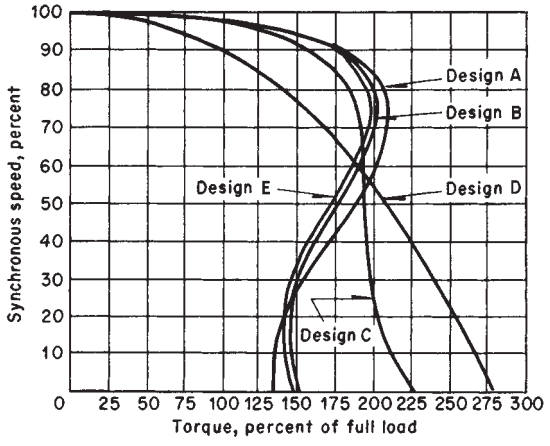


FIG. 29-2 Typical speed versus torque curves for various NEMA-design squirrel-cage induction motors. (See Table 29-2 for an explanation of design types.)

When making any economic analysis, care should be taken to be certain that the efficiency ratings of all motors being considered are on the same basis. While this should not be a problem for motors rated 1 to 500 horsepower as covered by the NEMA Standards for efficiency marking, it is common practice for several different test methods to be used when measuring the efficiency of motors rated over 500 horsepower. A particular test method may need to be selected by the test facility on the basis of available test equipment and power supply. All test methods that may be used to test any one motor will not necessarily give the same result for efficiency.

Further incentives to use energy-efficient motors are provided by various cost rebate programs offered by utilities based on horsepower rating and efficiency level. Another factor that will have a significant impact is the Energy Policy Act of 1992, in which the U.S. Congress established limits on the lowest level of nominal efficiency that certain classes of motors of standard design can have after 1997.

Control or **starting** of squirrel-cage induction motors normally consists of applying full voltage to the motor terminals. The speed-torque curves in Fig. 29-2 are based on full voltage throughout the speed range from start to run. The specific motor design determines the amount of starting current. However, if the motor is a typical standard (NEMA A or B) design, the starting current may be estimated at 6 to 6.5 times normal full-load current with full voltage applied. For NEMA Design E, it may be estimated at 8 to 9 times normal full-load current with full voltage applied. Particularly for large motors, this starting inrush current may cause an undesirable voltage dip which can shut down other equipment, temporarily dim lights, or even initiate malfunctions in sophisticated controls on the power system. For these conditions various alternatives exist.

1. *Reduced-voltage starting.* A reactor, resistor, or transformer is temporarily connected ahead of the motor during start to reduce the current inrush and limit voltage dip. This is accompanied by reduced starting torque. For reactor or resistor start, the torque decreases as the square of current; for transformer start, the torque decreases directly with line current. The reactor, resistor, or transformer can be adjusted to give a proper balance between torque and current.

TABLE 29-2 Characteristics and Typical Applications for Squirrel-Cage Induction Motors

	NEMA A and B	NEMA C	NEMA D	NEMA E
Starting torque	Normal	High	High	Normal
Running slip	Low	Low to medium	High	Low
Efficiency	Normal	Normal	Low	High
Applications	Pumps	Electrical stairways	Punch presses	Pumps
	Compressors	Pulverizers	Crushers	Compressors
	Fans	Conveyors		Fans
	Machine tools			Machine tools
	General use			General use

2. *Star-delta starting.* A delta-connected motor is reconnected in Y form for starting, thus applying 57.7 percent voltage to each phase winding. This results in a developed torque of $(0.577)^2$, or only 33 percent. There is no means of adjustment; therefore, this method is useful only for loads requiring less than one-third of the motor's normal starting and accelerating torques.

3. *Part-winding starting.* This method employs a motor with two sets of windings, only one of which is energized during start. Torque and current are both roughly 50 percent. Two small contactors (starting switches) are used instead of one large one, and no reactors or transformers are required. The disadvantages are the fixed value of available torque and the harmonic disturbances from possible winding unbalance, causing deviations in the speed-torque curve and therefore possible failure to accelerate.

Braking and regeneration are possible with squirrel-cage motors. The direction of rotation is determined by the sequence or phase rotation of the power supply. If two leads on a three-phase motor are interchanged, the rotation reverses. If this occurs during operation, the motor will come to a rapid stop and reverse. Power is removed at standstill for effective braking. For estimating only, this plug-stop torque is approximately equal to starting torque. The braking time can be estimated by

$$t = WK^2 n/308T \qquad (29\text{-}11)$$

where t = time, s
WK^2 = inertia, lb·ft^2
n = running speed, r/min
T = torque, lbf·ft

To convert pound-square feet to kilogram-square meters, multiply by 0.0421; to convert revolutions per minute to radians per second, multiply by 0.1047; and to convert pound-force-feet to newton-meters, multiply by 1.356.

These estimates are frequently inaccurate because of second-order effects such as rotor saturation and harmonics. If the application is at all critical, the motor manufacturer should be consulted.

Regenerative braking occurs at speeds above synchronous-motor speed resulting from an overhauling load or from switching from high to low speed on multispeed motors. The action is similar to normal motor operation except that the slip is negative. The motor acts as an induction generator, delivering energy to the power source. If a power source such as a gas expander or a downhill conveyor is available, regenerative braking is an effective method of regulating speed, conserving energy, and starting the driven (driving) machine. An induction generator can deliver power to the source about equal to its rating as a motor. Regenerative braking can be used only on power systems capable of absorbing the generated energy and of supplying magnetizing excitation (reactive power) for the motor.

Direct-current dynamic braking utilizes direct current applied to the stator winding. Alternating-current power is first removed by opening the motor contactor or starter; direct current is then applied by a second contactor. The direct current produces a stationary magnetic flux, in contrast to the normal rotating ac field. The rotor bars cut this field, inducing currents which react with the dc flux to develop braking torque. Braking effort is easily varied by adjusting the amount of direct current. A desirable feature of this method for standard motors is the relatively soft braking effort at full-load speed, reducing impact; further, the braking effort typically increases as speed drops, reaching a maximum near zero speed. Braking torque at standstill is zero; however, maximum torque occurs at such low speed that static friction is usually sufficient to prevent coasting. Peak braking torques can be high; so shafts, gearing, couplings, etc., should be checked. Caution should be exercised because frequent starting and stopping cause excessive heating.

Synchronous Alternating-Current Motors These motors run in exact clock synchronism with the power system. For most modern power systems, these are truly constant-speed motors.

In the conventional synchronous motor a rotating magnetic field is developed by the stator currents as in induction motors. The rotor, however, is different, consisting typically of pairs of electromagnets (poles) spaced around the rotor periphery. The rotor field corresponds to the field produced by the ac stator having the same number of poles. The rotor or field coils are supplied with direct current; the magnetic field is therefore stationary with respect to the rotor structure. Torque is developed by the interaction of the rotor magnetic field and the stator current (in-phase component). Under no-load conditions and with appropriate dc field current, rotor and stator magnetic-field centers coincide. The voltage applied to the stator winding is balanced by an opposing voltage generated in the stator by the rotor field (induced), and no ac power current flows. As load is applied, the rotor tends to decelerate momentarily, causing a shift of rotor position with respect to the ac field. This shift produces a difference between the applied and induced voltages; the voltage difference causes current to flow; the current reacts with the rotor magnetic flux, producing torque.

Synchronous motors should not be started with the dc field applied. Instead they are started as induction motors; bars, acting like a squirrel-cage rotor, are embedded in the field-pole surface and connected by end rings at both ends of the rotor. These damper bars also serve to damp out oscillations under normal running conditions. When the motor is at approximately 95 percent speed (depending upon application and motor design), direct current is applied to the field and the motor pulls into step (synchronism). Because the damper bars do not affect the synchronous-speed characteristics, they are designed for starting performance. This provides flexibility in the accelerating characteristics to meet specific application requirements without affecting running efficiency and other synchronous-speed characteristics. The rotor design of a squirrel-cage motor, on the other hand, must be a compromise between starting and running performance. The dc field is usually shorted by a resistor during starting and contributes accelerating torque, particularly near synchronous speed.

Power-factor correction is an important feature of synchronous motors. Conventional synchronous-motor power factors are either 100 or 80 percent leading. Leading-power-factor machines are used frequently to correct for the lagging power factor of the remaining plant load (such as induction motors), preventing penalty charges on power bills. Even 100 percent power-factor motors can be operated leading at reduced loads. An advantage of synchronous motors over capacitors is their inherent tendency to regulate power-system voltage; as voltage drops, more leading reactive power is delivered to the power system, and, conversely, as voltage rises, less reactive power, in contrast to capacitors for which the reactive power decreases directly in proportion to the voltage drop squared. The amount of leading reactive power delivered to the system depends on dc field current, which is readily adjustable.

Field current is an important control element. It controls not only the power factor but also the pullout torque (the load at which the motor pulls out of synchronism). For example, field forcing can prevent pullout on anticipated high transient loads or voltage dips. Loads with known high transient torques are driven frequently with 80 percent power-factor synchronous motors. The needed additional field supplies both additional pullout torque and power-factor correction for the power system. When high pullout torque is required, the leading power-factor machine is often less expensive than a unity-power-factor motor with the same torque capability.

Direct-current field excitation is supplied by various means. A dc generator (exciter) is often used either directly coupled to the motor shaft, belt-driven off the motor shaft (seldom used), or driven by a separate small motor (exciter motor-generator set). Direct-coupled and belt-driven exciters are always associated with a single motor and are controlled by adjustment of the exciter field. Motor-generator-set exciters may supply one or more synchronous motor fields. For reliability, several motor-generator sets may be paralleled to supply multiple motor fields; in such a case the exciter voltage is usually fixed (e.g., 125 or 250 V), and the individual synchronous-motor fields are controlled by motor field rheostats (much larger than exciter field rheostats). Static (rectifier) exciters are also used for single-motor or multimotor excitation. Special rectifiers are required to avoid damage from surge voltages on pullout. These exciters, rotating or static, require brushes and slip rings to conduct direct current to the rotating field structure.

Another concept is **brushless excitation,** in which an ac generator (exciter) is directly coupled to or mounted on the motor shaft. The ac exciter has a stator field and an ac rotor armature which is directly connected to a static controllable rectifier on the motor rotor (or a shaft-mounted drum). Static control elements (to sense synchronizing speed, phase angle, etc.) are also rotor-mounted, as is the field discharge resistor. Changing the exciter field adjusts the motor field current without the necessity of brushes or slip rings. Brushless excitation is suitable for use in hazardous atmospheres, where conventional brush-type motors must have protective brush and slip-ring enclosures.

Because of the more complicated design and the necessity for a field power supply, synchronous motors are typically applied only in large-horsepower ratings (several hundred horsepower and larger); synchronous motors over 59,680 kW (80,000 hp) have been built. With their latitude in size and characteristics and their important inherent high power factor and efficiency, synchronous motors are applied to a wide variety of drives. Engine-type motors (without shaft or bearings) are used almost exclusively to drive large low-speed reciprocating compressors. Other typical applications include jordans, compressors, pumps, ball and rod mills, chippers, crushers, and grinders. Speeds as low as 80 r/min are practical; the top speed is limited by the rotor structure and is dependent on horsepower. The approximate limit for 1800 r/min is 2238 kW (3000 hp); for 1200 r/min it is 29,840 kW (40,000 hp).

Synchronous speeds are calculated by Eq. (29-10). Speeds above the limits given are obtained through step-up gears; large high-speed centrifugal compressors are examples. Two-pole (3600 r/min at 60 Hz) synchronous motors can be built but are uneconomical in comparison with geared drives.

ALTERNATING-CURRENT MOTORS, MULTISPEED

Squirrel-cage induction motors are inherently single-speed machines, but multispeed operation can be obtained by reconnecting the stator windings of motors designed for this purpose.

Two-Winding Motors These motors illustrate the simplest concept. The two separate stator windings (three-phase or two-phase only) are designed and wound for a different number of poles. For example, one winding may be four poles (1800 r/min at 60 Hz) and the other six poles (1200 r/min at 60 Hz). Only one winding is connected at a time. This method is used for speed ratios other than 2:1. Since the two windings are independent, a large number of speed combinations is possible. The two windings are not necessarily of equal capacity.

Two-winding motors may be built for constant torque, variable torque, or constant horsepower. Constant-horsepower motors are capable of handling the same horsepower at both speeds (i.e., higher torque at the low speed). Constant-torque motors can handle the same load torque at either speed (e.g., conveyor drives). Variable-torque motors are designed for loads in which load torque varies as the square of speed and horsepower varies as the cube of speed. Typical applications are as follows:

Variable torque	Constant torque	Constant horsepower
Fans	Conveyors	Machine tools
Centrifugal pumps	Feeders	
	Reciprocating compressors	

Single-Winding Consequent-Pole Motors These motors can be used when the low speed is one-half of the high speed. They are available as three-phase only. The specially designed winding is regrouped by external reconnection (motor control) to obtain the desired speed. A 2:1 speed ratio only is obtainable by this method; speeds such as 3600/1800, 1800/900, and 1200/600 are obtainable. Variable-torque, constant-torque, and constant-horsepower designs are available with torque characteristics as discussed under "Two-Winding Motors." The control for two-speed single-winding motors is more complicated than for the two-winding control.

Four-Speed, Two-Winding Squirrel-Cage Motors These motors are built by combining the preceding two methods. The stator winding is composed of two consequent-pole windings. Each winding gives two speeds with a relation of 2:1 to each other. The standard 60-Hz speed combinations are 1800/1200/900/600 r/min and 1200/900/600/450 r/min. The three torque-capability designs of variable torque, constant torque, and constant horsepower are also available in these four-speed motors.

Pole-Amplitude-Modulated Induction Motors These are single-winding squirrel-cage motors with any combination of poles or speeds (e.g., 8/10 poles or 900/720 r/min or as wide as 4/20 poles or 1800/360/min). They are smaller and lighter than equivalent two-winding machines. The entire winding works at both high and low speed, resulting in greater thermal capacity and higher efficiency. The basic principle is that one frequency acted on (modulated) by another produces new frequencies equal to the sum and difference of the two. Thus, a six-pole field modulated by a two-pole field produces a four- and an eight-pole field. The four-pole field can be eliminated by proper winding geometry. Such a motor runs at six-pole speed (1200 r/min, 60 Hz) when connected normally and at eight-pole speed (900 r/min) when half of the coils are reversed to produce the two-pole modulation.

In the preceding discussion of multispeed ac motors note that only induction motors are considered. These have no discrete physical rotor poles, so that only the stator-pole configuration need be modified to change speed. To operate multispeed, a synchronous motor would require a distinct rotor structure for each speed. Thus multispeed is practical only for squirrel-cage induction motors.

ALTERNATING-CURRENT MOTORS, WOUND-ROTOR INDUCTION

Wound-rotor induction motors operate on the same principle as squirrel-cage motors. However, as the name implies, the rotor has windings rather than bars, and these windings are connected to shaft-mounted slip rings. Brushes riding on the slip rings are connected to external resistance or short-circuited. Wound-rotor motors have an additional dimension of flexibility in the **variability of external rotor resistance.** Rotor resistance affects the shape of the speed-torque curve; increasing resistance decreases the speed at which maximum torque occurs. Figure 29-3 illustrates this effect as resistance is increased from zero external resistance (at top) to a very high value (extreme left).

Reduced-speed operation reduces efficiency. **Efficiency** is approximately equal to speed expressed as a percentage of synchronous speed. Thus at 75 percent speed, about three-fourths of the motor

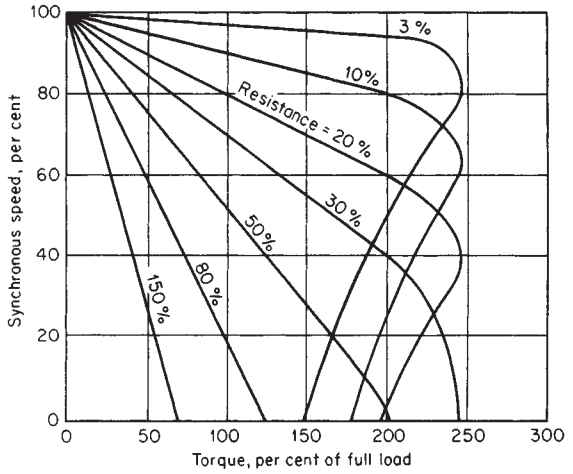


FIG. 29-3 Typical speed versus torque curves for a wound-rotor induction motor with varying amounts of external secondary (rotor) resistance. Resistance values are based on resistance at 100 percent torque and zero speed = 100 percent.

input goes to the load; the other quarter is dissipated in the rotor resistance. The external resistance is sized to get rid of this heat. Further, in accelerating a load to operating speed, the heat generated in the rotor resistance is equal to the energy required to accelerate the load (inertia plus friction). The rotor resistance (internal or external) must have capacity to store this heat, since accelerating time is typically too short to allow any significant heat dissipation.

These characteristics of wound-rotor motors determine their **scope of application.** They can accelerate very-high-inertia loads, such as crushers, by using a large external resistance to absorb the heat. Loads sensitive to shock-accelerating torques may also be accelerated softly by inserting a high starting rotor resistance; this effect is used, for example, to take up slack in gears. Wound rotors are also used to handle loads like punch presses and car crushers, for which extreme transient peak loads are supplied by the mechanical-system inertia, allowing the system to slow down during these peaks; permanent external rotor resistance provides this soft characteristic. Wound-rotor motors are also used to provide adjustable-speed drives for pumps, cranes, and other loads when precise speed regulation is not required. Reduced-speed losses are not very significant for pump loads; the percent efficiency is low at reduced speed, but the torque and load horsepower are dropping rapidly. If torque is proportional to speed squared, the maximum rotor-resistance losses never exceed 10.5 percent of the full-speed load (occurs at 70 percent speed and efficiency, 50 percent torque, 35 percent load horsepower, and 30 percent losses, thus 10.5 percent losses based on full load at full speed).

Control of wound-rotor motors, as discussed, can be effected by adjusting the external secondary (rotor) resistance either in steps or continuously by liquid rheostat (this method is seldom used). Commonly when secondary resistance is varied to adjust speed or torque or to control acceleration, multiple resistance steps are used. These steps may be switched manually (typically a drum switch) or electrically by contactor.

In addition to secondary resistance control, other devices such as reactors and thyristors (solid-state controllable rectifiers) are used to control wound-rotor motors. Fixed secondary reactors combined with resistors can provide very constant accelerating torque with a minimum number of accelerating steps. The change in slip frequency with speed continually changes the effective reactance and hence the value of resistance associated with the reactor. The secondary reactors, resistors, and contacts can be varied in design to provide the proper accelerating speed-torque curve for the protection of belt conveyors and similar loads.

Saturable reactors, which are adjustable by a small dc signal, have also been used for both primary (stator) and secondary (rotor) control. In the primary they control motor voltage and therefore torque. In combination with fixed secondary resistors and feedback from a tachometer, this system can be used for precise speed and torque control of cranes, hoists, etc. Even reversing can be accomplished by using two saturable reactors in each of two (of three) phases. Other combinations of fixed or saturable reactors in the primary and/or secondary, all combined with secondary resistors, provide a wide range of capabilities and flexibility for the wound-rotor motor.

Thyristors have been replacing saturable reactors; they are small, efficient, and easily controlled by a wide variety of control systems. A modern crane control drive uses fixed secondary resistors and two sets of primary thyristors (one set for hoist, one for lower). With tachometer feedback for speed sensing, the control for the motor provides speed regulation and torque limiting in both directions, all with static devices. A wide variety of control systems is possible; the control should be designed for the specific application.

DIRECT-CURRENT MOTORS

Direct-current motors are adjustable in speed over a wide range. Further, efficiency is high over the entire speed range, unlike wound-rotor motors, in which efficiency is roughly proportional to speed. This flexibility is attained at the expense of additional complexity and cost.

Direct-current motor fields are on the stator. The rotor is the armature. The magnetic field does not rotate like the field in ac machines. Current in the armature reacts with the stator field to produce torque.

The armature windings generate a voltage opposite to the applied voltage as they cut the magnetic field. The difference between the terminal voltage and the generated voltage (counterelectromotive force) applied to the armature resistance produces armature current. Torque is proportional to armature current and magnetic flux. Counterelectromotive force is almost equal to the applied voltage, so the speed can be changed by changing the applied voltage; the speed can also be changed by varying the field current.

$$E = V + IR \quad \text{or} \quad I = (E - V)/R \tag{29-12}$$

$$V = kn\phi \tag{29-13}$$

where E = applied voltage, V
V = counterelectromotive force (generated voltage), V
R = armature resistance, Ω
I = armature current, A
k = constant dependent on motor design
n = speed, r/min
ϕ = magnetic-field flux

Generated voltage is proportional to the magnetic-flux cut; so a motor must change speed to generate the same counterelectromotive force if the field current is changed.

Direct-current motors are connected in several ways. Shunt motors have armature and field connected in parallel. This connection provides almost constant speed regardless of the applied voltage. If the voltage drops, the counterelectromotive force also drops because of the reduction in field strength. Speed can be changed by varying the field current and/or armature voltage independently. Increasing armature voltage increases speed; increasing field current decreases speed.

Series motors have their armature and field windings connected in series; both carry the same current. The speed depends on both voltage and load. Torque is the product of armature current and magnetic field; both are dependent on current. For any specific load torque, the current is constant and speed is proportional to applied voltage. If, however, the load changes, the speed also changes. A 50 percent drop in load torque reduces the motor current to 70 percent, making the product of armature and field current 50 percent. The reduced field current decreases counterelectromotive force, and the motor speed increases by 40 percent. Because of this characteristic, series motors overspeed severely if unloaded. Series motors are suitable for constant-horsepower applications with a wide speed range,

such as machine tools. They are also used for traction drives (e.g., shuttle cars and locomotives), some cranes, hoists, and elevators.

Compound-wound dc motors have both series and shunt fields. The addition of a small series field helps provide the proper amount of no-load to full-load speed regulation or droop. Shunt or compound-wound motors are applied widely to many adjustable-speed drives. They are important for drives requiring accurate speed regulation and adjustment.

A dc motor's inherent speed-torque curve can be varied widely by adjusting the relative amounts of shunt and series fields. The series field may also be connected to aid or buck the shunt field. The usual practice is to connect the series field so that it adds to the shunt field (cumulative compound), which gives a stable, drooping speed with increasing load.

The great flexibility of dc motors both through inherent design characteristics and through the way in which they are operated makes them ideally suited to adjustable-speed drives, particularly regulated drive systems.

ADJUSTABLE-SPEED DRIVES

One of the oldest adjustable-speed drives is the **Ward-Leonard system.** This consists of an ac to dc motor-generator set and a shunt or compound-wound dc motor. Speed is adjusted by changing the generator voltage. A functional equivalent of this drive uses an adjustable-voltage rectifier feeding a dc motor. This system has only one rotating machine in contrast to the three of a conventional Ward-Leonard system.

Modern static controllable rectifiers such as thyristors respond almost instantaneously to control signals and are adaptable as the power supply to the most critical regulated-drive systems. The sensing and regulating system can be designed to hold speed, speed differential, tension, torque, current, acceleration and deceleration, etc., or any required combination. For example, a drive may be speed-regulated with torque limit or speed-regulated with acceleration and/or deceleration regulated or limited.

Typical applications for adjustable-voltage, adjustable-speed dc drives include winders, paper machines and auxiliaries, blending systems, feeders, extruders, calendars, machine tools, range and slasher drives, cranes, hoists, shovels and draglines, and an almost unlimited variety of drives requiring the flexibility and efficiency possible with direct current.

Mechanical adjustable-speed drives are used when a high degree of regulation is not required. One drive consists of a constant-speed ac motor driving the load through V belts and variable-pitch pulleys. The speed range can be as high as 8:1. It is available up to 18.6 kW (25 hp). Speed adjustment is either manual or remote with a motor drive for the adjustment. Speed regulation from no load to full load is normally 3 to 6 percent. Efficiency is high over the entire speed range since there are no slip losses.

Electromagnetic drives are simple adjustable-speed ac drives with efficiency comparable with that of wound-rotor motors. This drive uses a magnetic slip coupling driven by a squirrel-cage motor. The slip is determined by the excitation current and the load. Efficiency is proportional to speed. Therefore, these drives are uneconomical for continuous low-speed high-torque operation but are ideal for fans and centrifugal pumps requiring little speed adjustment when torque decreases rapidly with speed and for controlling acceleration. Electromagnetic drives are functionally equivalent to hydraulic couplings.

RectiFlow adjustable-speed drives use both a wound-rotor motor and a dc motor connected to the same shaft. The rotor winding of the wound-rotor motor is connected to a rectifier. The dc rectifier output supplies the dc motor. Semiconductor-rectifier developments make this a practical, high-efficiency adjustable-speed drive for applications up to several hundred horsepower. Since the rotor losses of the wound-rotor motor are used to produce shaft power and are not dissipated in a resistor, the efficiency of these drives is high over the entire speed range. A typical 223.8-kW (300-hp) RectiFlow drive operating over a 3:1 speed range has an efficiency of more than 83 percent over its operating range. RectiFlow adjustable-speed drives are suitable for high-torque low-speed drives such as extruders, mixers, pumps, fans, and kilns.

A modification of this basic drive system uses solid-state rectifiers and thyristors to convert the wound-rotor, variable-frequency slip power first to direct current and then to line-frequency power (60 Hz in the United States). This in turn is fed back to the power system as useful energy.

Adjustable-frequency alternating current can be used with squirrel-cage or synchronous motors for adjustable-speed drives. A typical application is small synthetic-fiber spinning drives which require multiple motors operating at constant speed. When precise synchronism between drives is required, synchronous-reluctance motors are used. These are squirrel-cage motors with flats or grooves on the rotor which form magnetic poles because of the change in magnetic path as the rotor position moves with respect to the stator field. This causes the rotor to rotate in exact synchronism with the stator field for light loads. The power source for these drives is either an ac generator driven by any adjustable-speed drive or a static inverter.

It should be noted that even motors as large as 60 MW have been equipped with these drives.

MOTOR ENCLOSURES

Except for areas with fire or explosion hazards (hazardous areas), motor enclosures are designed to provide protection to the internal working parts. The development of improved insulating materials and finishes has affected the required degree of protection and consequently the design and classification of enclosures. Examples of several types of enclosures are shown in Fig. 29-4.

Open, dripproof is the standard enclosure for induction, high-speed synchronous, and industrial dc motors. This design is useful for most indoor and many outdoor applications. Dripproof construction provides good mechanical protection to the internal working parts of the motor and prevents the entrance of dropping liquids and heavy dirt particles. However, it does not protect against airborne moisture, dust, or corrosive fumes. **Guarded** machines have all openings protected to prevent objects more than 12.7 mm (½ in) in diameter from entering the motor. **Splashproof** motors are not affected by water or by solid particles striking or entering the enclosure at an angle less than 100° from the vertical.

Weather-protected, type I is the next degree of protection for larger motors. Such a motor is defined as "an open machine with its ventilating passages so constructed as to minimize the entrance of rain, snow, and airborne particles to the electric parts" (NEMA Standard MG-1, "Motors and Generators"). All openings are restricted against passage of a 19-mm- (¾-in-) diameter rod. Some modern insulation systems are completely satisfactory for most outdoor applications.

Weather-protected, type II motors are recommended for large sizes when a higher degree of protection and longer life are desired. They have extensive baffling of the ventilating system so that the air must turn at least three 90° corners before entering the active motor parts [maximum air velocity, 3.05 m/s (600 ft/min)]; thus, rain, snow, and dirt carried by driving winds are blown through the motor housing without entering the active parts.

Totally enclosed motors offer the greatest protection against moisture, corrosive vapors, dust, and dirt. Totally enclosed fan-cooled (TEFC) motors are the obvious choice rather than *weather-protected* below 186.5 kW (250 hp). Their internal and external ventilating air are kept separate; external air never gets inside except for the small amount that enters by breathing.

TEFC motors have both an internal fan for circulating air within the motor and an external fan for forcing the air through or over the motor frame or heat exchanger. Small motors [approximately 2.238 kW (3 hp) and below] do not require ventilating fans; these totally enclosed nonventilated motors are similar to TEFC with the fans omitted.

Separate forced ventilation is required for some applications (for example, adjustable-speed drives which operate at low speed); these must depend on an external ventilation. This classification includes *open externally ventilated* machines, *open pipe-ventilated* machines,

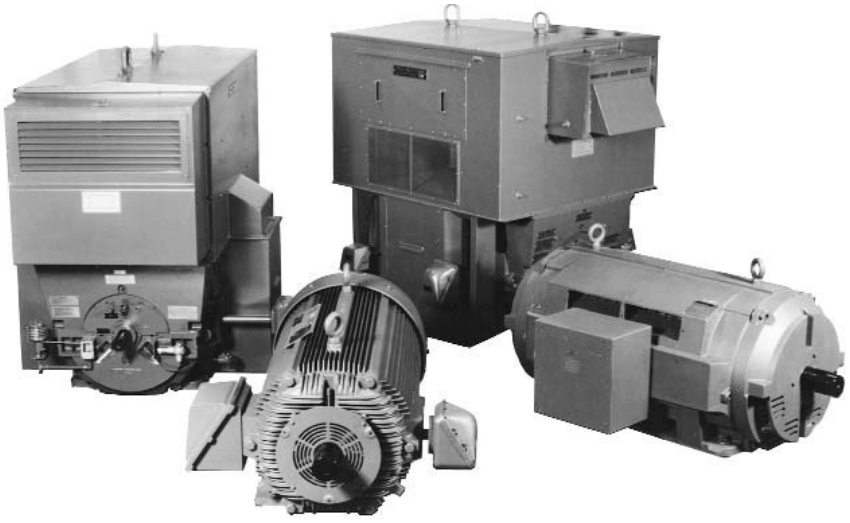


FIG. 29-4 Examples of open dripproof, totally enclosed fan-cooled, and weather-protected motor enclosures. (*Photo courtesy of Reliance Electric Company, Cleveland, Ohio.*)

and *totally enclosed pipe-ventilated* machines. In corrosive or hazardous areas, safe or clean air ventilates the motor.

Enclosed motors with air-to-water coolers cost much less than TEFC motors above 373 kW (500 hp); in large synchronous-motor ratings, they cost even less than weather-protected, type II. Large enclosed synchronous machines with coolers for mounting in the motor foundation are frequently supplied at lower cost than motors with integral-mounted coolers.

Fire or explosion hazards require special motor enclosures. Hazards include combustible gases and vapors such as gasoline; dust such as coal, flour, or metals that can explode when suspended in air; and fibers such as textile lint. The kind of motor enclosure used depends on the type of hazard, the type and size of motor, and the probability of a hazardous condition occurring. Some available enclosures are explosionproof motors, which can withstand an internal explosion; force-ventilated motors cooled with air from a safe location; and totally enclosed motors cooled by air-to-water heat exchangers and pressurized with safe air, instrument air, or inert gas.

MOTOR CONTROL

The basic functions of motor starters are:

1. Normal "start-stop" control of the motor.
2. Protection of the motor.
3. Protection of the electrical supply system in the event of a motor or motor-feeder short circuit. The fault must be cleared from the rest of the system to prevent further trouble.
4. Electrical isolation to provide accessibility for maintenance.
5. Provision for other control such as master sequence control, protective shutdown devices (e.g., bearing overtemperature, overtravel, pump high pressure, remote control, etc.).

Types of Starters

High Voltage and Low Voltage The electrical industry has standardized the distinction between high voltage and low voltage at 600 V. Below 600 V the common system voltages in use in the United States are 120, 208, 240, 480, and 600 V. Above 600 V, the standard nominal system voltages commonly in use are 2400, 4160, and 6900 or 7200 V. Higher voltages are available, but the motor cost is usually prohibitive.

For low-voltage starters below 600 volts, the same starters are used for any voltage, since there is only one insulation class.

For high-voltage motor-starting applications, there are several classes of insulation: 2500, 5000, 7500, and 15,000 V. The conventional control-type high-voltage motor starter is available for 2500- or 5000-V service. For voltages higher than this, switchgear must be used.

The construction of high-voltage starters employs much greater clearances and provides additional safety features such as grounded barriers between the high- and low-voltage sections of the starter. Extensive mechanical and electrical interlocking is also used for additional safety.

One of the major differences between high- and low-voltage starters is the amount of power handled. An approximate dividing line is 149.2 kW (200 hp). This, however, is not a fixed and rigid rule.

Line Starters and Combination Starters A line starter consists of a contactor (motor-starting switch) and motor-overload relays. Contactors are capable of carrying and interrupting normal motor-starting and -running currents; they are not, however, normally capable of interrupting short-circuit currents. They must be backed up by fuses or a circuit breaker for this function.

When a disconnect switch, circuit breaker, or set of fuses is included in the same enclosure as the contactor, the starter is then called a **combination starter.** In addition to the fault-current-interrupting function, the breaker or fuses serve as the disconnecting device. Figure 29-5 illustrates schematically combination starters of various types. The latch is arranged to open the disconnect before the door can be swung open. There are also provisions for padlocking the disconnect open with the door closed so that maintenance work on the motor may proceed in safety.

Manual and Magnetic Starters Manual motor starters are operated by hand. The simplest type of manual starter is a snap switch with no overload protection, used only for motors of 1.492 kW (2 hp) and smaller, usually single-phase motors with integral overload protection.

Magnetic motor starters are similar in function to manual starters except that they are solenoid-operated. They are available up to 3730 kW (5000 hp). One of the main advantages is the convenience of electrical operation. Start-stop push buttons can be located anywhere. When automatic or remote operation is needed, magnetic starters are essential.

Comparison of Switchgear and Contactor-Type Control Frequently switchgear is used for motor control, particularly for large high-voltage motors. Switchgear (Fig. 29-6) must be used for motors

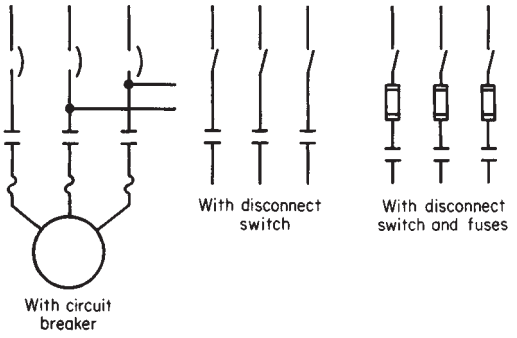


FIG. 29-5 Simplified schematic diagram of a combination line starter with a circuit breaker as the fault interrupter and disconnect. Alternative fuses and disconnect switch are shown as substitutes for the circuit breaker.

larger than 3357 kW (4500 hp)* at 4160 or 4600 V or 1865 kW (2500 hp)* at 2300 V and for all motors above 5000 V. Switchgear consists of circuit breakers and protective relaying. Circuit breakers are electrical switches designed primarily for their ability to interrupt short-circuit currents. This is one of the major differences from contactors, which are designed principally to handle starting and running currents. Contactors normally depend on a set of fuses or a circuit breaker to handle major faults (short circuits).

Contactors are designed for frequent operation. Circuit breakers are designed for far fewer operations and therefore are never used as motor starters when repetitive operation is required. A typical example of frequent operation is mine-hoist service, in which the motor must be reversed at the end of every hoisting or lowering operation; contactors would be used.

* 3730 kW (5000 hp) and 2051 kW (2750 hp) for unity power factor synchronous motors.

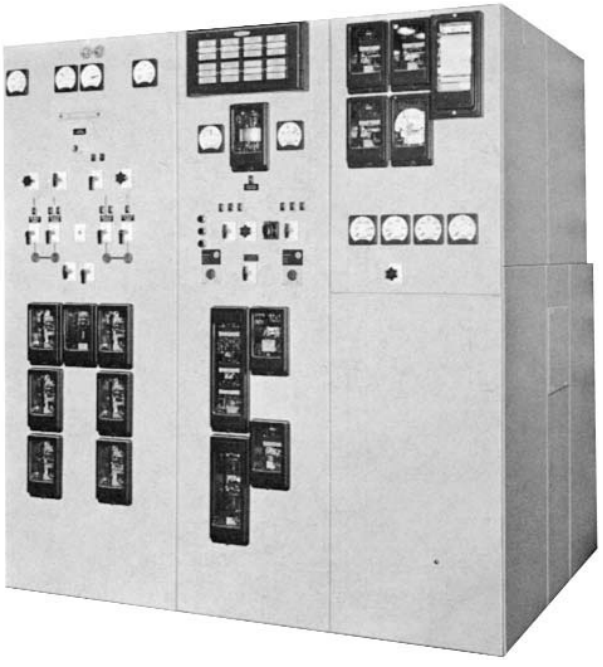


FIG. 29-6 Typical lineup metal-clad switchgear including motor starters and protective relaying.

High-voltage ac control-type (contactor) motor starters use fuses to provide short-circuit interrupting capacity. One disadvantage of fuses is that only one fuse may blow. This leaves single phase applied to the motor. Motors will continue to operate with single-phase power but can overheat even with less than rated current flowing. In contrast to contactors, circuit breakers are three-pole devices: a fault on one phase will trip all three, minimizing the single-phasing problem.

Centralized Control As mentioned previously, motor starters may be located either at the motor or at some remote point. Frequently they are grouped at a location convenient to the source of power. The feeders radiate from this point to the individual motor loads. A convenient method is the control-center modular structure for low-voltage control, into which are assembled motor starters and other control devices. The individual starters can be drawn out of the structure for rapid, easy maintenance and adjustment. With this construction it is easy to change starter size or add additional starters. All the starters are in one location, so that interwiring is simple and easy to check. Auxiliary relays, control transformers, and other special control devices can also be included. See Fig. 29-7.

Motor Protection Money spent for motor-protective devices can be compared to insurance, in which premiums depend on the protected value when the protected value is the cost of the motor, the cost of anticipated repairs, or the cost of downtime, lost production, and, in some cases, contingent damage to other equipment.

Overload Protection Overload relays for protecting motor insulation against excessive temperature are located either in the motor control or in the motor itself. The most common method is to use thermal overcurrent relays in the starter. These relays have heating characteristics similar to those of the motor which they are intended to protect. Either motor current or a current proportional to motor-line current passes through the relays so that relay heating is comparable to motor heating.

Standard thermal overcurrent relays located in the starter have some disadvantages. They cannot detect abnormal temperatures in the motor caused by blocked ventilation passages or high ambient temperature at the motor. They are also likely to trip out unnecessarily in locations where the control enclosure is at a higher temperature than the motor. Motors are normally ventilated with external air so that their ambient temperature is the ambient temperature of the surrounding air. However, control enclosures are not freely ventilated, so their internal temperature can become quite high if they are located in a sunny location. High-current relays are sometimes used to avoid this difficulty. This prevents the motor from being tripped out unnecessarily because of high ambients inside the control enclosure, but the motor will be improperly protected during cool weather and overcast days and at night. Ambient-temperature-compensated relays should be used in these situations.

Some overload-protection schemes measure motor-winding temperature directly; various methods are used. Small single-phase motors are available with built-in overload protection. A thermostat built into the motor senses motor-winding temperature directly.

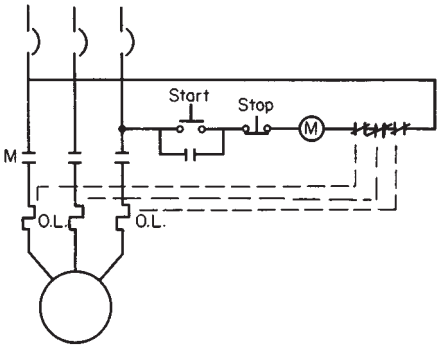


FIG. 29-7 Schematic diagram of a combination starter, showing a simple control scheme.

When the motor overheats, the thermostat opens, interrupting motor-line current. Pilot thermostats mounted on the windings of larger motors trip the motor starter rather than interrupt line current. This method gives good protection for sustained overloads, but because of the thermal time lag between the copper winding and the thermostat it may not provide adequate protection for stalled conditions or severe overloads.

Temperature detectors embedded in the motor winding give close, accurate indication of motor temperature. Both conventional resistance temperature detectors (RTD) and special thermistors (highly temperature-sensitive nonlinear resistors) are used. With appropriate auxiliaries these devices can indicate or record motor temperature, alarm, and/or shut down the motor.

Short-Circuit Protection Short circuits must be removed promptly to avoid severe damage at the fault and to avoid disturbances to the rest of the electrical system. Short-circuit protection should be set as low as possible so that tripping action is initiated quickly. Motor-starting inrush current sets a limit on how low short-circuit devices may be set. For squirrel-cage ac motors, instantaneous short-circuit tripping should be initiated at about 7 to 10 times full-load running current. This gives an adequate margin above the normal inrush of approximately 6 times full-load current. Modern low-voltage combination starters are available with adjustable instantaneous circuit breakers which can be set just above motor-starting current.

High-voltage contactor-type motor controls depend on power fuses for short-circuit protection. The fuses are coordinated with the overload relays to protect the motor circuit over the full range of fault conditions from overload conditions to solid maximum-current short circuits.

Locked-Rotor Protection Under locked-rotor (stalled) conditions the rotors of large synchronous and squirrel-cage motors are the most likely motor elements to be damaged by overheating. The rotor's heating is not related to stator heating during startup. Therefore for large motors it is common practice to use separate devices or characteristics to protect against running overloads and locked-rotor conditions if the overload and short-circuit protective devices cannot be coordinated to handle this condition for the specific motor characteristics.

Synchronous-motor rotor frequency can be detected because the rotor field circuit is available. Special control schemes have been devised which take into account both speed and induced rotor current in providing locked-rotor and accelerating protection.

Undervoltage Protection If a power outage occurs, it is necessary to remove motors from the line to prevent excessive starting current surges on the electrical system when voltage is reestablished. It is also unsafe to have drives starting indiscriminately when electrical service is reestablished. Conversely, it may be desirable to leave the motors connected during short voltage dips; this is time-delay undervoltage protection. Instantaneous undervoltage protection disconnects the motor as soon as the voltage drops appreciably. This is satisfactory if continuity of operation is relatively unimportant. It is inherent in low-voltage magnetic starters when a power loss drops out all contactors as soon as a voltage dip occurs. If time-delay undervoltage protection is desired for these controls, time-delay relays must be added to the standard control circuit. Because circuit breakers do not drop out on a voltage dip, undervoltage relays are necessary.

Reverse-Phase Protection Reverse-phase relays are used on some large motors to prevent their starting when the electrical-system phase rotation is reversed because of improper wiring or maintenance. They are also used as undervoltage and voltage-balance relays. Individual relays may be applied to each motor in place of the undervoltage relay, or one relay may be operated off a bus for several motors. Individual relays are more expensive but more reliable, particularly when motor circuits are changed frequently. This type of protection is normally supplied only on high-voltage switch-gear-type starters.

Phase-Current Balance Protection Three-phase ac motors will usually continue to operate on single phase. Single phasing is serious on large ac motors because of the severe rotor heating it causes. Single-phase conditions cannot be detected by measuring voltage; a running motor acts as a generator so that, even under single-phase conditions, motor terminal voltage is nearly normal. Current-balance relays give a positive indication of system current unbalance and single-phase operation. Normally one three-phase relay is used for each motor. The use of these relays is restricted to large motors [approximately 1119 kW (1500 hp) and larger] when the value of the equipment protected justifies the cost of this protection.

Adequate single-phase protection is provided on low-voltage ac motor starters by three overload relays, which are now standard. Rotor heating is not particularly a problem on smaller motors which have more thermal capacity, but it is important to protect the stator windings of these machines against burnout.

Differential Protection Differential protection is applied to detect internal motor faults quickly and limit damage. The cost of this protection is justified on large motors [1119 kW (1500 hp) and above], for which limiting the motor damage may save the cost of this additional protection many times over.

Motor differential protection is one of the most sensitive forms of large-motor protection available. Figure 29-8 illustrates the basic principles involved. All six leads (both ends of all three windings) are brought out to terminals. The electric current entering each winding and the current leaving that winding pass through the same current transformer in opposite directions. If everything is normal, these currents are equal and no current is induced to the current transformer winding. If a phase-to-phase (winding-to-winding) or winding-to-ground short circuit occurs, the currents do not balance, current is induced in the current-transformer winding, and the differential relay operates instantaneously, shutting down the motor. Because of its sensitivity and speed, this system limits motor damage, minimizing repair costs and downtime.

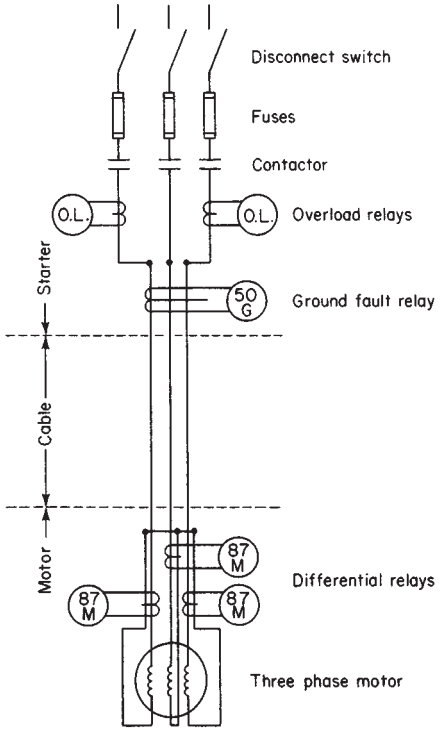


FIG. 29-8 Typical high-voltage ac motor starter illustrating several protective schemes: fuses, overload relays, ground-fault relays, and differential relays with the associated current transformer that act as fault-current sensors. In practice, the differential protection current transformers are located at the motor, but the relays are part of the starter.

Ground-Fault Protection High-voltage motors (2300 V and above) should be protected with ground-fault relays if the power source is grounded (see Fig. 29-8). This scheme includes a large-diameter current transformer (CT) encircling all three motor leads. Short-circuit current to ground flows through the CT to ground and returns to the power source external to the CT; this unbalance induces current in the CT and ground relay to shut down the motor. With this protection only two overload relays and two line CTs (rather than the standard three) are required, so the additional protection is very economical. It cannot be used, however, unless the power source is grounded.

Both differential and ground relaying detect ground faults. Ground-fault protection is located at the starter and protects the cable and the motor; differential CTs are located at the motor and protect the motor only. Economic priorities indicate ground-fault protection first, adding differential protection when justified by potential savings in downtime and repair costs.

Surge Protection High-voltage motors should be equipped with surge-protection apparatus consisting of a set of three lightning arresters and three surge capacitors. Potentially damaging voltage surges or spikes can be generated on the power system by switching operations, certain faults, or lightning. The surge capacitors slope off these steep front voltage spikes, and the lightning arresters limit the peak voltage; both functions are essential for adequate protection. Surge protection should be located at each motor's terminals for maximum protection, although in many instances one set of surge equipment is connected to the electrical bus serving several motors.

Special Control

Reduced-Voltage Starting Reduced-voltage starting is used to reduce system voltage dip. Voltage dips must be limited; otherwise, they may drop other motors off the line, cause synchronous motors on the system to pull out of step, or cause objectionable lamp flicker.

Resistor and reactor starting are the simplest methods of reduced-voltage starting. These systems require two contactors or breakers and a set of reactors or resistors, in contrast to the single-contactor full-voltage starter. The starting contactor closes first, connecting power to the motor terminals through the reactors. The impedance in the circuit reduces the motor terminal voltage and the starting current. As the motor approaches full speed, the running contactor closes, shorting out or bypassing the reactors, applying line voltage to the motor terminals. Starting current is reduced in proportion to the reduction in motor voltage. However, torque is proportional to the square of motor voltage, so starting torque is reduced far more than starting current.

If a greater reduction in line current is required for starting ac motors than is possible with reactor starting, autotransformers may be used. Because of transformer action, the reduction in motor-starting torque is directly proportional to the reduction in line current. Table 29-3 compares reactor and autotransformer starting with respect to line current and torque. Other, less commonly used methods of reduced-voltage starting include part-winding starting and star-delta starters.

TABLE 29-3 Effects of Reduced Voltage Starting*

Starter type	Motor voltage	Motor current	Line or source current	Motor torque	Source voltage dip
Design	100	100	100	100	0
Actual full voltage	80	80	80	64	20
Reactor:					
0.8 tap	67	67	67	45	17
0.65 tap	56	56	56	31	14
0.5 tap	44	44	44	20	11
Autotransformer:					
0.8 tap	69	69	55	48	14
0.65 tap	59	59	38	35	10
0.5 tap	47	47	24	22	6

*Values shown are in percent of design or normal starting values and are calculated for an arbitrary hypothetical power source whose voltage would dip by 20 percent if full-voltage starting were used.

Synchronous-Motor Starters Except for the addition of the synchronous-motor field-application panel, control schemes are identical for both synchronous and induction motors. Excitation is not applied to synchronous motors until they reach approximately 95 percent speed. Field current should be applied when the field poles are in proper space relationship to the stator's rotating magnetic field. Both speed and position are indicated by the ac voltage generated in the field winding. The frequency is directly proportional to slip and therefore indicates speed; the magnitude and polarity of the generated wave indicate position relative to the armature field. When the proper speed and position are detected, field current is applied. When reduced-voltage starting is employed, the ac starting sequence is completed before the application of field current.

Multispeed Alternating-Current Starters Multispeed induction motors are either two-winding motors, single-winding motors with consequent-pole connection or pole-amplitude-modulated motors (see subsection "Alternating-Current Motors, Multispeed"). The starters for two-winding, two-speed motors are quite simple; they consist of two standard single-pole, single-speed starters in the same enclosure with appropriate mechanical and electrical interlocks so that the two contactors cannot be closed simultaneously.

Two-speed, single-winding motors, either consequent-pole or pole-amplitude-modulated, require a three-pole and a five-pole contactor mechanically and electrically interlocked. Three- and four-speed, two-winding motors require a combination of two-speed, single-winding and two-speed, two-winding starters. Further modifications are possible by making these multispeed-control-reversing.

Secondary Control of Wound-Rotor Motors Wound-rotor motors may be effectively reduced-voltage-started or have their speed controlled by using external secondary resistance. The addition of resistance into the secondary circuit of a wound-rotor motor reduces the starting current and affects the speed under load conditions.

When external secondary resistance is used for improved starting characteristics, short-time-rated resistors are employed. As the motor accelerates, steps of resistance are cut out on a time or current basis to give the desired accelerating torque and current characteristics.

When external secondary resistance is used for speed adjustment, the resistors may be either infinitely adjustable (e.g., liquid rheostats) or adjustable in steps (if fine speed adjustment is not required).

Direct-Current Motor Control Control for dc motors runs the gamut from simple manual line starters to elaborate regulating systems. Only the starting problems are considered here since variable-speed drives and regulating systems are discussed elsewhere.

The major differences between ac and dc starters are necessitated by the commutation limitation of dc motors, which is the ability of the individual commutator segments to interrupt their share of armature current as each segment moves away from the brushes. Normally 250 to 275 percent of rated current can be commutated safely. Since motor-starting current is limited only by armature resistance, line starting can be used only for very small [approximately 1492-W (2-hp)] dc motors. Otherwise, the commutator would flash over and destroy the motor. External resistance to limit the current must be used in starting to prevent this.

Manual rheostats can be used in series with the motor armature for the current-limiting function. If the rheostat has ample thermal capacity, it can also be used to vary speed. If this system is used, interlocks should be included to prevent closing of the contactor unless maximum resistance is in the circuit.

Magnetic starters short out the starting resistance in one or several steps based on time, current, or speed. The number of steps depends on the size of the motor and the application. Current-limit acceleration is used frequently for high-inertia drives which require a long accelerating time. Motor current is sensed by a current relay which actuates the shorting contactors in sequence as the current drops. Time-limit acceleration is more common. The motor accelerates in a definite time by shorting out the starting resistor steps in timed sequence.

RECIPROCATING ENGINES

STEAM ENGINES

The advent of electric motors, steam turbines, and other drivers has relegated the steam engine to a minor position as an industrial driver. It does have the advantages of reliability and operating characteristics that are not obtainable with other drivers but also the disadvantage of bulkiness and oily exhaust steam.

In the simple **nonexpanding engine** as used with direct-acting reciprocating pumps, steam is admitted over the entire stroke and does not expand in the cylinder, resulting in relatively low efficiency. Control is simple, and pump speed is regulated by steam throttling. By proper selection of the steam and pump piston sizes, these pumps can deliver high shutoff pressures, which can be used to overcome temporary blockages of pipe lines or for other situations requiring high pressure of short duration.

The higher-efficiency **expanding steam engines** use cutoff valves to limit steam admission to the cylinder during the initial part of the stroke, and the expansion occurs during the remainder of the stroke. Larger engines use several cylinders in series to achieve full expansion. Although this type of engine can be controlled with throttling valves, the preferred method is to change the cutoff point, thus eliminating throttle-valve losses and permitting change in output from zero to maximum design power. Thus almost complete expansion is achieved at part loads and overloads, resulting in efficient operation for the full range of loadings.

Although this type of engine is efficient, it is limited by its inability to utilize low-vacuum exhaust and/or high steam pressures and temperatures commonly used by steam turbines. With low steam pressures [2068 kPa (300 psig)] and low vacuums [88 kPa (26 in Hg)] a steam engine will have a better efficiency than a steam turbine of the same rated power. For each cutoff setting an engine will develop the same torque at all speeds, with steam consumption and power output directly proportional to speed. All other drivers, except certain dc electric motors, require the same input for constant torque at varying speeds.

Changing the cutoff-point setting will allow an engine designed for one gas to operate efficiently on any other gas (limited only by corrosiveness, fouling, etc.). This characteristic favors the use of reciprocating engines when it is necessary to expand gases efficiently in process applications in which the composition is variable. A further advantage is that an engine is the only driver with essentially zero gas consumption at zero speed while developing full torque and maintaining full process pressures. A combination of an expansion engine driving an oil brake provides a high-efficiency refrigeration effect over a wide range of process conditions, with the process controllers throttling the oil flow in the oil brake.

The **uniflow design** reduces cylinder condensation and also allows greater expansion ratios per cylinder (see Figs. 29-9 and 29-10). Steam is admitted during the start of the power stroke and after cutoff is expanded to a pressure slightly higher than the exhaust pressure. At the end of the stroke the piston uncovers the exhaust ports of the cylinder with partial steam and discharges into the exhaust system. The steam remaining in the cylinder is compressed during the return piston stroke, maintaining higher average cylinder temperatures in order to reduce steam condensation during admission.

To reduce friction and cylinder wear oil is injected into the cylinders of engines, and to maintain lubricity cylinders of engines on low-temperature services are warmed. Oil causes foaming in boilers and can contaminate low-temperature process streams. Therefore, in steam plants oil is usually removed from the condensate. By using carbon or plastic rings similar to those used in oil-free reciprocating compressors, oil for lubrication can be omitted. But these rings are not as reliable as lubricated cast-iron piston rings.

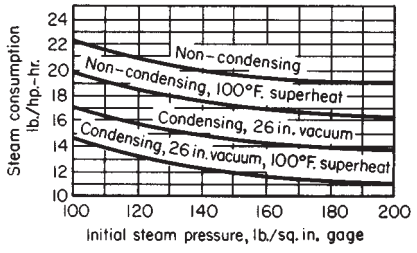


FIG. 29-9 Steam consumption of a 400-hp uniflow engine. To convert pounds per horsepower-hour to kilograms per kilowatthour, multiply by 0.6084; to convert pounds-force per square inch to kilopascals, multiply by 6.89.

INTERNAL-COMBUSTION ENGINES

Internal-combustion engines range in size from small portable gasoline engines to over 14,914 kW (20,000 hp) diesels for ship propulsion. They are usually designed for particular industrial applications and to meet specific objectives as to weight per horsepower, reliability, and operating conditions.

All internal-combustion engines fall into two main types, namely, four-cycle and two-cycle engines. These engines may be further classified as (1) gasoline or gas engines (Otto cycle), in which a spark plug is used to ignite a premixed fuel-air mixture; (2) diesel engines (diesel cycle), in which high-pressure compression raises the air temperature to the ignition temperature of the injected fuel oil; (3) dual-fuel or gas-diesel engines, in which the fuel is a combination of gas and oil in any desired ratio, provided that at least 5 percent oil is used at all times; and (4) trifuel engines, which can operate as dual-fuel or as straight gas engines by replacing the oil-injection system with a spark plug for ignition.

Design Characteristics Internal-combustion engines involve consideration of the following design features: (1) **Compression ratio,** an increase of which usually increases engine efficiency but also results in higher average cycle temperatures and therefore hotter cylinders, piston heads, and rings which increases the difficulty of piston lubrication. (2) **Piston speed,** which is a major overall criterion of engine design since power rating is proportional to piston speed. Reciprocating forces and lubrication problems increase with piston speed. (3) **Brake mean effective pressure** (bmep), which is an overall measure of the output of an engine frame; bmep increases with compression ratio and degree of supercharging, and, in general, high values are associated with modern high-efficiency industrial engines. It is also the overall criterion for bearing loadings and average piston-head and cylinder temperature. (4) **Engine rating,** which is proportional to the product of piston speed and bmep. Acceptable values of piston speed and bmep are more dependent on industrial usage than on the type of engine. (5) **Supercharging,** which connotes means for increasing the inlet manifold air pressure above ambient

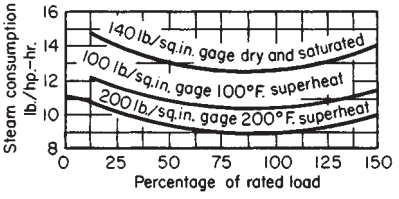


FIG. 29-10 Steam consumption of a uniflow engine with 27.5-in vacuum. To convert pounds per horsepower-hour to kilograms per kilowatthour, multiply by 0.6084; to convert pounds-force per square inch to kilopascals, multiply by 6.89.

pressure. (6) **Turbocharging,** which applies to the expansion of the hot exhaust gases through a turbine to drive the supercharging compressor. Since power output is proportional to inlet manifold air pressure, supercharging provides increased power output and usually higher efficiency. Highly supercharged engines may require an air cooler between the compressor and inlet manifold.

Engine size is usually in terms of power rating (horsepower) rather than the physical size of the engine frame. Frame size is determined by the diameter of the cylinder bore, length of stroke, and number of cylinders. The power rating of a given frame varies with industrial practice and usage; accordingly, automobile engines are designed to develop between 0.54 and 0.95 hp/in^3 of piston displacement, while industrial diesels are limited to 0.045 to 0.60 hp/in^3.

Engine rating reflects industrial practice. Automobile engine rating is the peak horsepower developed on a test stand, whereas industrial engine rating is usually in terms of continuous load.

Industrial engines are made in a wide variety of frame sizes, each offered at several power and speed ratings. The same engine frame might drive either a 900-kW generator at 900 r/min or a 600-kW generator at 600 r/min by using lighter pistons and special parts for the higher-speed application. An engine originally designed for 746 kW (1000 hp) may be uprated to 820 kW (1100 hp) by higher compression heads and further to 984 kW (1320 hp) by supercharging. Thus one frame can cover a power range from 447 kW (600 hp) (60 percent speed) to 984 kW (1320 hp). An engine frame can also be designed for different output by varying the number of cylinders; for example, a 10-cylinder 2610-kW (3500-hp) engine will develop 1566 kW (2100 hp) and 2088 kW (2800 hp) at the same efficiency with six and eight cylinders respectively. This enables a manufacturer to use the same basic design, tools, and fixtures for a variety of ratings.

Maximum rating is the horsepower capability of the engine that can be demonstrated within 5 percent at the factory corrected to standard conditions. Standard conditions in this case are at sea level with barometric pressure of 760 mm (29.92 in) Hg and a temperature of 15° C (59° F). **Intermittent** is the horsepower and speed capability of the engine which can be utilized for approximately one hour, followed by about an hour of operation at or below the continuous rating. Many engine operators choose to run their engines continuously in this rating area, trading shorter maintenance periods for increased earnings. **Continuous** is the horsepower and speed capability of the engine which can be utilized without interruption or load cycling. This can extend for months or years of operation if the engine is equipped for on line lube oil and filter changes. **Intermittent** and **continuous** ratings are at standard conditions of 746 mm (29.38 in) Hg and 30° C (86° F); turbocharged engine ratings are applicable to at least 760 m (2500 ft) elevation above sea level without derating.

It is important that atmospheric conditions at the installation site be specified, since engines operate with very little excess combustion air and consequently maximum power output is proportional to air density.

Operating Characteristics The operating characteristics of internal-combustion engines are basically the same regardless of fuel used or whether the engine is two- or four-cycle. To vary the speed and/or load-carrying capacity, which can range from zero to full torque for all speeds within the operating range, it is necessary only to vary the fuel input. Large engines use a governor to control the fuel-input rate and maintain constant speed under variations of load. With auxiliary instrumentation the governor can be used as a controller of power or process. Starting, stopping, and operation from a remote location are made possible by instrumentation that will also shut down an engine in the event of loss of cooling-water or lubricating-oil flow.

Starting is accomplished by rotating the engine at a speed sufficient to achieve ignition and self-sustained operation. Small engines are started with electric motors or smaller hand-starting engines, and large engines are provided with special valving whereby some of the engine cylinders can be operated as air motors, utilizing high-pressure air to rotate the engine. Starting motors are usually sized at 5 to 10 percent of the engine rating. Starting-air requirements are 0.014 m^3 (0.5 ft^3) (free air)/hp stored at a pressure of 1723 kPa (250 psig) to 2068 kPa (300 psig). Usually three starts per successful firing are assumed for sizing the starting air compressor and air-storage vessel.

Operating characteristics of engines are also influenced by **service requirements.** Automotive engines must develop maximum torque at lower speeds for hill climbing; marine engines are required to develop full torque only when the propeller is at full speed; generator drivers run at a single speed and therefore require maximum possible efficiency at all loads for this speed; and reciprocating compressors at constant pressure require full torque over the entire operating-speed range, thus presenting an engine-instability problem at reduced speeds. The engine must be selected to meet these service requirements.

Supercharging is employed primarily to improve engine efficiency or power output, but part-load performance and rate of response to load changes depend on the type of supercharging system used. Some systems result in supercharged engines having the same torque-speed characteristics and rate of response to load changes as nonsupercharged engines, while other systems result in poorer or better response and in different speed-torque characteristics.

Maintenance and Reliability Preventive maintenance requires that all engines be shut down at periodic intervals for inspection and repair. For properly maintained heavy-duty engines availability is over 97 percent, with maintenance costs of $2.50 to $5 per horsepower-year and lubricating-oil consumption of 1 to 2 gal/hp·year.* While this represents a high degree of reliability, outages of heavy-duty engines are more frequent than those of electric motors or steam turbines.

Satisfactory engine performance is assured by maintaining a minimum log that allows comparison of present characteristics with past records of (1) cylinder exhaust, cooling water, and supercharger exhaust temperature for similar loadings, (2) running sounds and smokiness of exhaust, and (3) engine efficiency and losses.

The minimum safety devices for an industrial engine are a governor and separate overspeed and low-oil-pressure trips. Engines operating in nonsupervised areas should be arranged to shut down in the event of cooling-water or lubricating-oil failures and for excessive exhaust or jacket-water temperatures. Engines operating in supervised areas should be provided with instruments for the operator to check performance.

Fuel Characteristics Fuels used in industrial engines of the internal-combustion type are usually derivatives of petroleum or else natural or manufactured gases. Alcohols and mixtures of gasoline and alcohol or benzol can also be used. A gas engine will operate satisfactorily on any gas which is free of dust, noncorrosive (i.e., less than 0.6 grains/ft^3), does not detonate, does not preignite during compression stroke, and produces enough heat on burning to develop power.

In general, the fuel must have a heat capacity of over 600 Btu/ft^3. Gasoline engines require, in addition, that the fuel will vaporize in the carburetor. Diesels will burn any fuel that can be injected, provided that it will burn under controlled conditions, possesses sufficient lubricity to lubricate the injection plungers, will supply enough heat, and is grit-free, containing less than 3 percent sulfur, 70 ppm vanadium, and 125 ppm vanadium pentoxide. Most diesel engines use either No. 2 or No. 5 fuel oil. The latter must be heated to a viscosity of 50 to 70 SSU [121°C (250°F) approximately] for proper injector lubrication and injection characteristics.

Gaseous fuels containing fractions whose ignition temperature is lower than that of methane may require the use of low-compression heads and a resulting derating of the gas engine.

The method of reporting fuel consumption varies among different industries and also among countries. Trade associations usually have recommended procedures. Thus the Diesel Engine Manufacturers

* For further details of industrial operating costs see *Annual Oil and Gas Engine Power Costs,* published by the American Society of Mechanical Engineers. Engine manufacturers will supply recommended schedules for preventive maintenance.

Association (United States) calculates efficiencies based on the lower heating value (LHV) for gas fuels and the higher heating value for oil fuels. It is general practice to report gas-engine performance in terms of British thermal units per horsepower-hour (LHV) and oil-engine performance in terms of pounds of fuel consumed per horsepower-hour. For electric power plants, fuel consumption is reported in terms of kilowatts. Auxiliaries included with engine-efficiency calculations vary with industry practice.

Fuel Economy and Heat Recovery The high overall efficiencies obtained by modern high-compression supercharged diesels or gas engines can be approached only by very large high-pressure reheat steam plants or by very complicated gas-turbine cycles. The following efficiencies (LHV) based on methane fuel for gas engines and oil fuel for diesel engines can be used for estimating fuel consumption: 63 kW (85 hp) to 298 kW (400 hp), 28 percent; 328 kW (440 hp) to 597 kW (800 hp), 32 percent; 597 kW (800 hp) to 2237 kW (3000 hp), 36 percent; and over 2461 kW (3300 hp), 41 percent.

Instead of working with efficiencies (Eff.) the term **brake-specific fuel consumption** (BSFC) is frequently used with liquid fuel engines. BSFC is expressed in g/kWh (lb/Hp·h) and assumes equal fuel or heating value (LHV) when comparing different engine performances. Using the relationship BSFC = 1/LHV × Eff and LHV = 43 MJ/kg (18,400 Btu/lb) for gasolines and diesel fuels, efficiencies can be calculated from Eff = 84/BSFC (Eff = 0.14/BSFC).

Plant fuel costs chargeable to power production can be reduced if heat losses can be utilized to provide process or other heating. Engine heat losses as percentages of heat input (LHV) are (1) lubricating-oil cooling, 5 to 7 percent available at 82° C (165° F); (2) jacket cooling, 17 to 30 percent available as 82° C water or with vapor-phase cooling as 103 kPa/ (15 psig) steam; (3) engine exhaust gases, 26 to 30 percent available with approximately half of this at sufficient temperature to generate 689.5 kPa/ (100 psig) steam in waste-heat boilers. Table 29-4 gives some heat-balance data for gas engines.

Vapor-phase cooling reduces the cost of the cooling system, increases heat recovery, and may result in improved engine efficiency.

At full speed fuel consumption decreases linearly with reduction in load, becoming at zero load almost one-third to one-fourth of full-load consumption and with no potential for heat recovery in the exhaust. Jacket-water heat losses decrease by 20 to 40 percent at zero load. Fuel consumption at rated torque is almost proportional to speed. At half speed exhaust recovery decreases to less than half, and jacket-water cooling becomes more than half of full-torque values.

Emission Control Internal cumbustion engines must meet national, state, and regional exhaust emission regulations. On an international scope, many countries have introduced emission regulations on stationary engines. These regulations not only vary from one location to the next, but they also tend to become more restrictive as time goes by. Further, as fuel costs rise, the economics of various emission control techniques are changing. Current emission control measures are given in Table 29-5.

Installation and Costs An engine installation includes auxiliary equipment necessary for operation, such as lubrication pumps and attendant storage, filtering and cooling equipment; jacket-water pumps with expansion tank and cooler; starting-air tanks and compressors; inlet-air piping and screens; exhaust-air piping and silencers or waste-heat boilers; a fuel system, which in the case of diesels would include a day tank, filters, pumps, heaters, and a main storage tank; ignition system or fuel-injection plungers; and cooling towers or radiators. Diesel engines operating on heavy residual fuel oils would have two-fuel systems, a heavy-fuel-oil system for normal operation and a light-fuel-oil system for starting and stopping.

Pipe-line and marine installations are frequently arranged so that the engine drives all its auxiliaries from the crankshaft by means of chains and V belts. But process-plant practice is to have all the auxiliaries independently driven, using standby pumps to minimize engine downtime.

Foundations should be designed to control **vibrating motion** resulting from reciprocating masses. Engine manufacturers will recommend the size of the foundation, but usually their recommendations do not take soil properties into account and are based on making the combined engine and foundation weight sufficiently large to limit vibration. When possible, foundations should be separate from the building structure. In many cases vibration of the engine will cause no damage; nevertheless, it is good practice to reduce it whenever possible. Even though vibration does not increase any forces in the engine, it can loosen pipe joints, nuts, etc.

Torsional vibration can also be a problem and results from pressure variations in the cylinders which can produce cyclic torques with harmonics ranging from half speed to 10 or 12 times running speed.

Table 29-6 gives costs for engine installation, which can be prorated to make preliminary estimates of installation costs.

To avoid operating difficulties, the torsional critical frequencies of the combined engine and driven equipment should be calculated or measured to assure that operating speeds are removed from these criticals or that vibration dampers are provided or that the equipment is designed for the resulting cyclic stresses.

The costs of both engines and auxiliaries are reasonably consistent on the basis of dollars per horsepower as long as essential details are

TABLE 29-4 Approximate Heat Balance for Gas Engines—5965 kW (8000 bhp)

	Two-cycle			Four-cycle		
	U.S. units	SI units		U.S. units	SI units	
	Btu/BHP·hr	kJ/kWh	%	Btu/BHP·hr	kJ/kWh	%
Heat Input (LHV)	6500	9196		6200	8772	
Useful Work	2545	3601	39.2	2545	3601	41.0
Cooling System	940	1330	14.5	1000	1415	16.1
Lubricating Oil System	292	413	4.5	300	424	4.8
Intercooler System	530	750	8.2	250	500	4.0
Exhaust	1540	2179	23.7	1685	2384	27.2
Radiation	650	920	10.0	200	283	3.2
Combustion	—	—	—	220	311	3.5

TABLE 29-5 Current Emission Reduction Measures

Type of engine	Emissions	Emission reduction measures
Gas-Otto-Engine 20 kW (27 hp) to 2,000 kW (2,685 hp)	NOx CO HC	Air/fuel ratio = 1- and 3-way catalytic converter Stratified charge technology (lean burn) and enhanced turbocharging Catalytic converter plus NH_3 injection
Diesel Engine 5 kW (7 hp) to 4000 kW (5400 hp)	NOx CO HC PM*	Small engines: Prechamber Midrange: Adjustment for maximum performance and fuel economy Large engines: Exhaust filter and catalytic converter with NH_3 injection
Diesel-Gas-Engine 300 kW (400 hp) to 8,000 kW (10,740 hp)	NOx CO HC PM*	Catalytic converter Catalytic converter with NH_3 injection

*Particulate matter (soot).

TABLE 29-6 Comparative Installation Costs of Integral-Engine Compressors for Pipeline Stations and Process Plants*

	Pipeline station	Process plant
A. Land and improvements	$ 459,200	$ 67,900
B. Structures	1,036,800	553,600
C. Testing	40,000	40,000
D. Equipment	8,183,000	6,053,750
Subtotal	9,719,000	6,715,250
Add 10% for overhead and undistributed field costs	971,900	671,525
Subtotal	10,690,900	7,386,775
Add 5% for contingencies	534,545	369,339
Total	11,225,445	7,756,114
Cost per horsepower	802	554

*10 units are assumed for a total of 10, 4 MW (14,000 hp). Basis year is 1993.

TABLE 29-7 Typical Cost of Engine-Driven Equipment (1994 basis)

	$/hp
Integral engine compressors:	
Uninstalled and without auxiliaries	334
Installed cost with auxiliaries and cooling water	541
Installed costs of large units with cooling water supplied from process	532
Diesel or gas-engine generators:	
Uninstalled	282
Installed	544

the same. Published figures on **installed engine costs** are often misleading, since with supercharging more power output can be obtained from the same size of engine, which also reduces cooling-water and foundation requirements. Pipe-line compressor costs frequently include piping, buildings, etc.; and in some process plants, cooling water which has been used and charged against process operation can be reused for engine cooling at no cost. It is obvious that general cost predictions must be used with caution unless their detailed basis is known. However, as preliminary figures, Table 29-7 may prove useful (1994 basis):

STEAM TURBINES

Steam turbines are divided into two broad categories: those used for generating **electric power** and general-purpose units used for driving pumps, compressors, etc., and frequently called **mechanical-drive** turbines.

Figure 29-11 illustrates in general the relationship of capability versus speed. At 1800 and 3600 r/min are the turboelectric generator drives with capability limits above the top of the chart. The majority of mechanical-drive applications are within the shaded area; capabilities above the solid line are special and unusual.

Inlet-steam pressure is usually in the range of 1723 kPa (250 psig) at zero superheat to 5860 kPa (850 psig) at 482° C (900° F). Some turbines have been built to operate at 35 kPa (5 psig) with zero superheat from a process exhaust. Pressures of 10,342, 12,410, and 16,547 kPa/(1500, 1800, and 2400 psig) are common for large turbine generators, and some operate at supercritical pressures of 24,131 kPa/(3500 psig) and 34,474 kPa (5000 psig). Power plants that generate steam with nuclear reactors generate saturated steam in the range of 1379 to 6895 kPa (200 to 1000 psig). Early units were 125 MW, but currently 250 to 1500 MW are the most common size. These units have multiple casings and 1.32-m-(52-in-) long blades in 1800-r/min exhaust stages.

TYPES OF STEAM TURBINES

Straight Condensing Turbine All the steam enters the turbine at one pressure, and all the steam leaves the turbine exhaust at a pressure below atmosphere.

Straight Noncondensing Turbine All the steam enters the turbine at one pressure, and all the steam leaves the turbine exhaust at a pressure equal to or greater than atmosphere.

Nonautomatic-Extraction Turbine, Condensing or Noncondensing Steam is extracted from one or more stages, but without means for controlling the pressures of the extracted steam.

Automatic-Extraction Turbine, Condensing or Noncondensing Steam is extracted from one or more stages with means for controlling the pressures of the extracted steam.

Automatic-Extraction-Induction Turbine, Condensing or Noncondensing Steam is extracted from or inducted into one or more stages with means for controlling the pressures of the extraction and/or induction steam.

Mixed-Pressure Turbine, Condensing or Noncondensing Steam enters the turbine at two or more pressures through separate inlet openings with means for controlling the inlet-steam pressures.

Reheat Turbine After the steam has expanded through several stages, it leaves the turbine and passes through a section of the boiler, where superheat is added. The superheated steam is then returned to the turbine for further expansion.

STAGE AND VALVE OPTIONS

The **single-stage, single-valve** turbine is the simplest turbine, and it sees the most varied application. There is a single governor valve in a steam chest, operated directly from a mechanical flyball governor. After passing through the valve, steam is expanded through the nozzles, where it gains velocity and momentum for driving the wheels by impulse action against the blades. The shaft is sealed by carbon rings. The sleeve bearings are ring-oiled. The majority of applications are below 1119 kW (1500 hp) and at speeds below 5500 r/min with 4137 kPa (600 psig) or lower steam pressure. By certain changes higher limits such as 1492 kW (2000 hp), 10,000 r/min, and 8274 kPa (1200 psig) can be made available.

The **multistage, single-valve turbine** is widely used for driving compressors and pumps in the range from 1119 to 4474 kW (1500 to 6000 hp). Figure 29-12 shows a section of a turbine of this type. The inlet end of this multistage turbine retains the general arrangement of bearing case, governor, and steam chest as used on the single-stage, single-valve turbine. The casing is extended to contain the added stages, and the last blade row and the exhaust opening are large in order to contain the volume of the exhaust steam at the low condensing pressure, which may be 6.9 or 13.8 kPa(a) (1 or 2 psia).

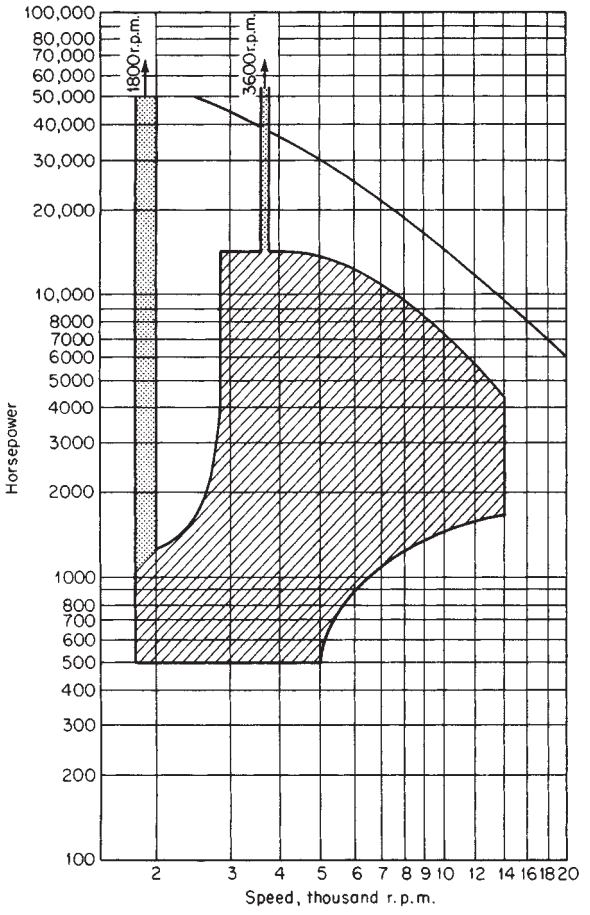


FIG. 29-11 Steam-turbine capability versus speed. To convert horsepower to kilowatts, multiply by 0.7457.

TYPES OF BLADES AND STAGING

Figure 29-13 illustrates a turbine stage in which steam at pressure p_1 enters the nozzle or stationary blade and expands to a lower pressure p_2, leaving the nozzle at a velocity of C_1. The rotating row is moving at a velocity μ so that steam enters the rotating row at a relative velocity w_1 and leaves the rotating row at a relative velocity w_2. The pressure on the exit side of the rotating row is p_3.

Depending upon the relationship between the pressures p_1, p_2, and p_3, the stage is classified as either impulse or reaction.

For an **impulse** (Rateau or Curtis) **stage,** p_2 is equal to p_3 or only slightly higher, and w_2 is slightly less than w_1 as a result of friction loss in the blade passage. The exit area a_r of a rotating row is 50 to 74 percent larger than the exit area a_s of the stationary row in order to pass the same quantity of higher-specific-volume steam.

The work done in the stage, which is the push of the steam on the blades, is the change in momentum of the steam as it alters direction from C_1 to C_2, using the peripheral projection of the velocities. Therefore, it is desirable for the angles α and β to be very small.

For a **reaction stage** the exit area a_r is reduced by reducing the angle β. This will increase the pressure p_2, possibly to midway between p_1 and p_3. The exit velocity w_2 is now greater than the blade entrance velocity w_1 because of the pressure drop from p_2 to p_3 through the blade passage. The reaction in a stage is expressed as a percentage of stage available energy.

Because of the smaller blade angle the reaction stage is more efficient than the impulse stage, but it requires more stages for the same pressure drop. This will increase the losses and the leakage, and the choice is generally close to a standoff.

A **Curtis stage** is an impulse stage that makes use of two rotating rows to absorb the energy in C_1 with a stationary reversing row between them. This comes about when C_1 is high compared with the wheel peripheral velocity μ, so that the exit velocity C_2 still has a lot of energy left in it. This energy is dissipated by adding a stationary row to reverse the flow and then putting it through an additional rotating row. It is universal practice for single-stage turbines when the ratio p_1/p_3 is in the range of 2 to 2.5 or greater. The two-row impulse (Curtis) stage is not as efficient as the single-row stage, owing to the higher losses encountered with the high steam velocities and repeated turning of the stream.

PERFORMANCE AND EFFICIENCY

The energy available in the steam is expressed in British thermal units per pound, or enthalpy. The velocity of the steam flow through the nozzle is calculated from

$$C_1 = 223.7\sqrt{\Delta h} \qquad (29\text{-}14)$$

where C = velocity, ft/s, and Δh = enthalpy drop from p_1 to p_2, Btu/lb. This is the same formula that is used for the spouting velocity of liquid in terms of head by introducing the mechanical equivalent of heat.

For calculation purposes the **efficiency of individual turbine stages** is plotted as efficiency versus velocity ratio μ/C_1, where μ equals wheel peripheral velocity. Figure 29-14 shows the relation between the three principal types of stages; each one has a peak efficiency at a certain ratio of μ/C_1. For the same revolution per minute, of course, the two-row stage takes the highest value of C_1 and the highest enthalpy drop. The reaction stage takes the lowest. The single-row impulse (Rateau) stage is in the middle. The reaction stage is denoted as 70 percent, because 30 percent of the enthalpy is allowed for expansion in the stationary row and 70 percent in the rotating row.

Steam Rate Enthalpy data can be obtained from Mollier diagrams or from steam tables (see Sec. 2), from which the **theoretical steam rate** can be calculated. For example, a throttle inlet condition of 4137 kPa (600 psig) and 399° C (750° F) gives an enthalpy of 3.2 MJ/kg (1380 Btu/lb), and if the end point is at 348 kPa (50 psig), then adiabatic expansion is to 2.69 MJ/kg (1157 Btu/lb). This gives 0.52 MJ/kg (223 Btu/lb) available, and the theoretical steam rate is calculated from the Btu equivalent per kilowatthour or horsepower-hour:

$$2544/223 = 11.4 \text{ lb steam/(hp·h)}$$

Theoretical-steam-rate tables are available as separate publications. Table 29-8 covers some common conditions.

The **actual steam rate** is obtained by dividing the theoretical steam rate by the turbine efficiency, which includes thermodynamic and mechanical losses. Alternatively, internal efficiency can be used, and mechanical losses applied in a second step.

Efficiency varies over a wide range, dependent upon the number of stages in the turbine. If steam conditions are assumed to be 4 137 kPa (600 psig) at 399° C (750° F) inlet and 13.8 kPa (2 psia) exhaust, Table 29-8 shows a theoretical steam rate of 3.47 kg/kWh (7.65 lb/kWh). With efficiencies that might be experienced for the given steam conditions with single-stage, five-stage, seven-stage, and nine-stage turbines, the actual steam rates would be as in Table 29-9.

From this table note that efficiency increases with the number of stages and that the increased number of stages corresponds to larger horsepower values. For each stage, as characterized by diameter and speed, there is a Btu drop that gives the best efficiency provided there is enough steam to fill the stage so that it operates with minimum friction and windage loss. Thus the nine-stage turbine is fine for 7.46 MW (10,000 hp), but it would not show up as well as a five-stage turbine at 0.746 MW (1000 hp) because the losses would increase with the light flow.

From the velocity diagram in Fig. 29-13 it is apparent that an increase in wheel peripheral velocity μ permits an increase in nozzle exit velocity C_1 without increasing C_2. Accordingly, a high-speed tur-

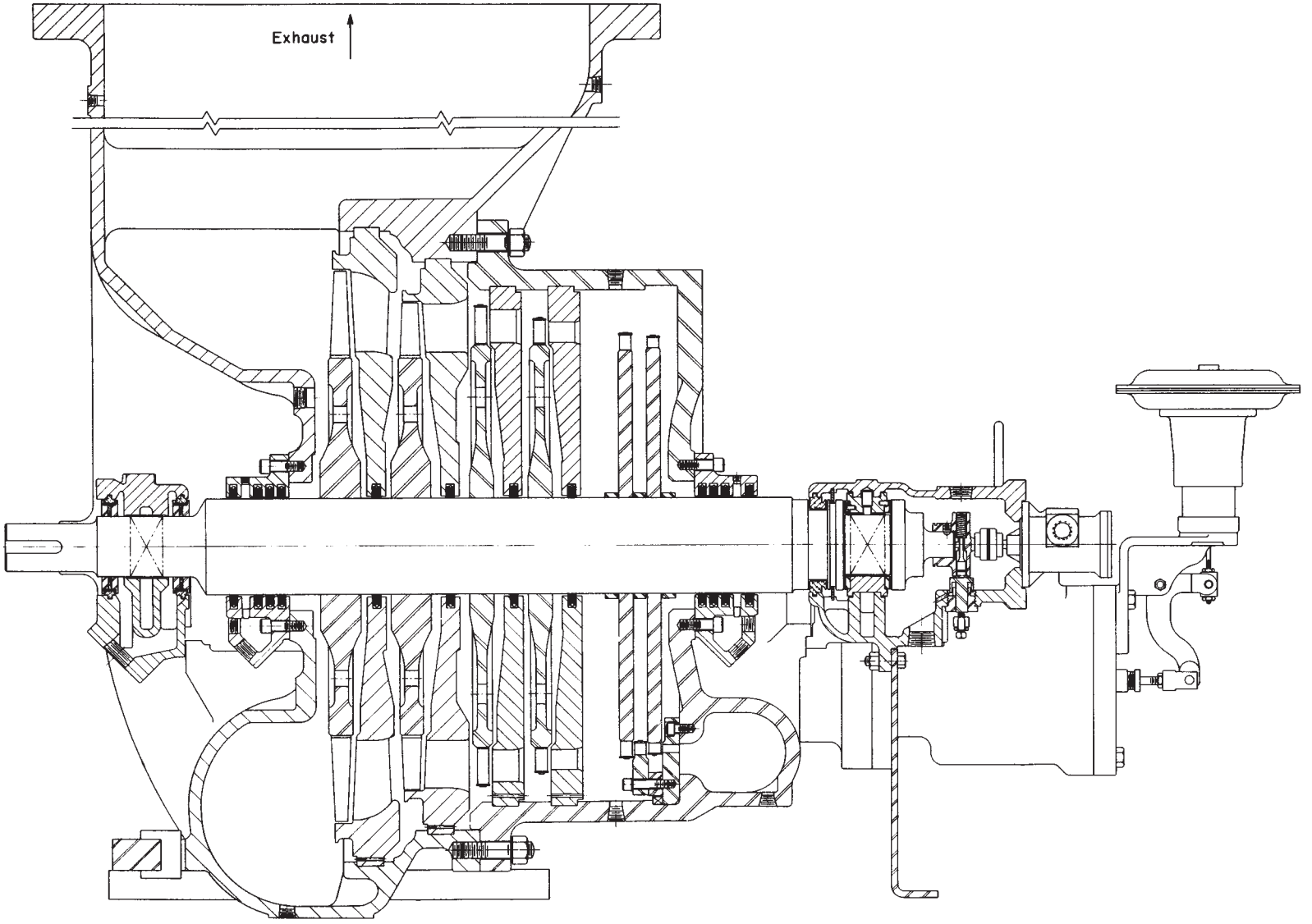


FIG. 29-12 Single-valve, multistage steam turbine. (*Elliott.*)

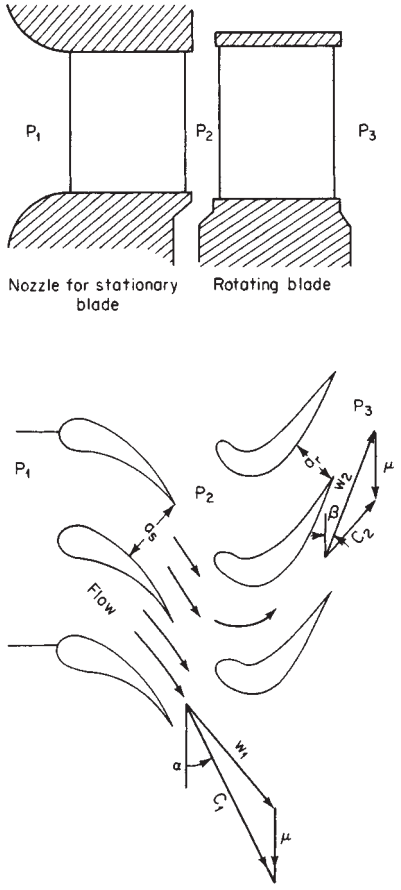


FIG. 29-13 Basic mechanics of a turbine stage.

bine can use more Btu per stage and will have fewer stages than a slow-speed turbine.

The leaving velocity C_2 is a measure of the unused energy. For best efficiency C_2 should have no radial component; C_2 should be straight axial. For all stages except the last one, C_2 represents a carryover to the next stage. For the last stage, C_2 is the velocity into the exhaust hood and is referred to as the leaving loss or exhaust loss.

The curves in Figs. 29-15 and 29-16 can be used for estimating **steam rates of single-stage turbines** by proceeding according to the following example. For steam conditions of 2760 kPa (400 psig) and 399° C (750° F) inlet and 5170 kPa (75 psig) exhaust, Table 29-8 gives theoretical steam rate as 20.59 lb/kWh. If the turbine is 300 hp and 4000 r/min, enter the top of Fig. 29-15 at 4000 and for a trial stop at 18-in-base diameter of turbine blading, then drop to TSR 20.59, and the base steam rate is 37 lb/hp·h. Next enter the top of Fig. 29-16 at 4000 r/min, and intersect 75 psig, then drop to 18-in diameter and find 8-hp loss. Total horsepower then is 308.5, and steam required is (308.5) (37.0) = 11,400 lb/h. By reading values for other diameters a selection table can be prepared, shown as Table 29-10.

From this table the most efficient unit can be selected and balanced against price. It is apparent that for 300 hp the 28-in diameter achieves no gain over the 22-in diameter because of the increase in horsepower loss. For 22 in versus 18 in the gain is small and may be offset by the higher price.

Steam rates for multistage turbines depend upon many more variables than do single-stage turbines and require extensive computation. Depending upon the type of turbine, single-valve or multivalve, general-purpose or generator-drive, condensing or noncondensing, with or without extraction, the manufacturers have shortcut procedures for estimating performance in their bulletins for the different types. As a general approximation the curve in Fig. 29-17 may be used, if one keeps in mind that an actual turbine may be several points above or below the curves, depending upon the use of optimum staging for efficiency or a compromise to meet price. Speed is also important; high speed at 373 kW (500 hp) may have high losses, while 7460 kW (10,000 hp) at 12,000 r/min may be above the curve. And steam pressure affects performance. The most efficient turbine is one in which speed, pressure, and steam flow combine to fill the blade path so that there are no partial-admission stages. For partial admission the nozzles do not fill the entire 360° arc because there is not enough steam for that many nozzles. Those portions of the blades which are spinning outside of the nozzle arc create friction and windage.

TURBINE CONTROL

A turbine may be speed-, pressure-, or process-controlled. Some of the terms used are defined as follows:

Speed-governing system includes the speed governor, the speed changer, the servomotor that moves the valves, and the governor-controlled valves.

Speed governor includes only those elements which are directly responsive to speed and position the other elements.

The **speed changer** is a device by means of which the set point may be varied.

Steady-state regulation is the change in sustained speed or pressure (expressed as a percentage of rated) when power or flow output is gradually reduced from rated value to zero.

TABLE 29-8 Theoretical Steam Rates for Steam Turbines at Some Common Conditions, lb/kWh

	Inlet conditions							
Exhaust pressure	150 lb/in² gage, 366°F, saturated	200 lb/in² gage, 388°F, saturated	250 lb/in² gage, 500°F, 94°F superheat	400 lb/in² gage, 750°F, 302°F superheat	600 lb/in² gage, 750°F, 261°F superheat	600 lb/in² gage, 825°F, 336°F superheat	850 lb/in² gage, 825°F, 298°F superheat	850 lb/in² gage, 900°F, 373°F superheat
2 in. Hg.	10.52	10.01	9.07	7.37	7.09	6.77	6.58	6.28
4 in. Hg	11.76	11.12	10.00	7.99	7.65	7.28	7.06	6.73
0 lb./sq. in. gage	19.37	17.51	15.16	11.20	10.40	9.82	9.31	8.81
10 lb./sq. in. gage	23.96	21.09	17.90	12.72	11.64	10.96	10.29	9.71
30 lb./sq. in. gage	33.6	28.05	22.94	15.23	13.62	12.75	11.80	11.07
50 lb./sq. in. gage	46.0	36.0	28.20	17.57	15.36	14.31	13.07	12.21
60 lb./sq. in. gage	53.9	40.4	31.10	18.75	16.19	15.05	13.66	12.74
70 lb./sq. in. gage	63.5	45.6	34.1	19.96	17.00	15.79	14.22	13.25
75 lb./sq. in. gage	69.3	48.5	35.8	20.59	17.40	16.17	14.50	13.51

NOTE: To convert pounds-force per square inch to kilopascals, multiply by 6.8948; to convert pounds per kilowatthour to kilograms per kilowatthour, multiply by 0.4536; °C = 5/9(°F − 32).

TABLE 29-9 Typical Stage Efficiencies for Steam Turbines at 600 psi Inlet Pressure and 750°F Inlet Temperature

Turbine design	Turbine hp	Internal efficiency, %	Exhaust enthalpy, Btu/lb	Δh,* Btu/lb	Steam rate
Single-stage	500	30	1245	135	7.65/0.30 = 25.5 lb/kw·hr
5-stage	1,000	55	1135	245	7.65/0.55 = 13.9 lb/kw·hr
7-stage	4,000	65	1090	290	7.65/0.65 = 11.75 lb/kw·hr
9-stage	10,000	75	1020	360	7.65/0.75 = 10.02 lb/kw·hr

NOTE: To convert horsepower to kilowatts, multiply by 0.7457; to convert British thermal units per pound to kilojoules per kilogram, multiply by 2.33.

*Based on inlet enthalpy = 1380 Btu/lb.

Speed variation is the total variation in speed from the set point and includes both dead band and oscillation.

Proportional-action governor is a governor with inherent regulation and a continuous linear relation between the input (speed change) and the output of the final control element, the governing valve.

Proportional-action governor with reset is a governor with inherent regulation so that the momentary output is proportional to input change, and subsequently a reset action initiated by the output acts on the speed changer or its equivalent to make the settled regulation less than the inherent regulation.

Isochronous governor is a floating-action governor that controls for constant speed. It is equipped with a dashpot or buffer to give momentary regulation for a speed-input change.

Control-System Components The three principal elements of a control system are the sensing device which measures the error as the deviation from the set point, means for transmission and amplification of the error signal, and the control output device in the form of a servo-operated valve. In the case of the **direct-acting flyball governor** (Fig. 29-18) these three elements are combined in the flyball element and the linkage that connects to the valve.

The centrifugal force of the weights is continually compared against the set point as established by the governor spring which opposes the force from the governor weights. For an increase in load the speed drops, and the weight force is reduced, which allows the spring to push the governor spindle to the left. The lever then pivots, and the valve moves to the right and opens to increase steam flow and torque. The feedback in the control is the resultant increase in speed to match the set point of the governor spring again and eliminate the error. This governor corresponds to NEMA Class A, 10 percent speed regulation, that is, 10 percent speed rise from full load to no load, and the governor weights must move out to close the valve.

The force required to position the valve and the specified regulation puts a practical limit on the direct-acting governor. Beyond this limit a servo is required. The servo requirement has three levels. The lowest level is for a single valve of the balanced type in Fig. 29-18 which may be controlled with less than 889.6 N (200 lb) force. The next level is a single valve with single seat of the venturi type; partially balanced it requires 3558.4 N (800 lbf) to 4448 N (1000 lbf) force. The top level is the multivalve bar-lift or the cam-lift valve gear, in which 8- and 10-in and larger oil servos are used in developing several thousand pounds-force.

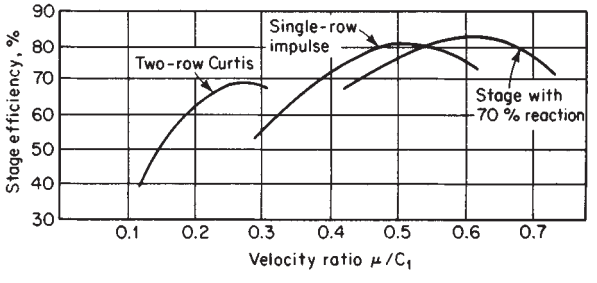


FIG. 29-14 Stage efficiency for different types of stages.

Speed-Control Systems The most common sensing element is mechanical; some systems are hydraulic or electronic. For valve positioner they all have a hydraulic servo as first choice, with an occasional choice of pneumatic for lighter loads.

Figures 29-19 and 29-20 illustrate two different **mechanical-hydraulic systems.** Figure 29-19 is a bar-lift steam chest with a heavy-duty hydraulic servo. The speed-sensing element is a flyball assembly attached to a rotating pilot. This rotating pilot sends a control-pressure signal that is proportional to speed to a bellows on the servo. A change in control pressure initiated through the rotating pilot by either speed or speed changer deflects the bellows and servo pilot valve. The servopiston position is proportional to the control pressure.

Figure 29-20 has a spring-return servo that finds application on single-valve turbines with a moderate valve force. For a speed change the rotating pilot sends an error signal through the dashpot to the servopiston. This is a dashpot-type isochronous governor; the error signal sees an instantaneous regulation due to the springs in the dashpot, but after the pressures have equalized through the needle valve, there is no resultant force change on the governor pilot. Control pressure is not proportional to speed; so the governor has zero regulation, also referred to as isochronous control. The setting of the needle valve determines the time required for the system to equalize after a disturbance. This may be several seconds.

Electrohydraulic speed control is in use for turbogenerators and mechanical drive applications because of accurate speed control and easy adaptation to computer operation and such remote control as automatic starting and loading. These same characteristics make it suitable in process plants. Figure 29-21 indicates the elements of electrohydraulic control. A pickup is mounted adjacent to a tooth wheel on the shaft. As the teeth move past the pickup, each tooth generates a small emf pulse. These pulses constitute a digital input to the amplifier. The amplifier performs three functions. The digital input is integrated to a dc level proportional to speed, it is amplified, and the amplified voltage level is matched against a set-point circuit. The differential output current is used to drive an electrohydraulic converter. The converter controls the pilot valve on a standard steam-chest servo. The converter shown puts out a control pressure proportional to current, and the pressure is applied to the bellows. Current electronic governor systems position the servo pilot valve directly.

Remote speed control or **process speed control** takes one of two forms. The remote signal may position the valve directly by acting on the valve stem or on the servo pilot. This action is independent of the governor. For this form of operation the governor is set for maximum operating speed and will take over in an emergency. The operation is referred to as preemergency. In the second type the remote signal acts on the speed changer or its equivalent to adjust the set point. The governor is now always in the circuit, and the unit is always speed-responsive.

The speed control operates the governing valve to maintain steam flow commensurate with load demand while holding speed essentially constant. For sudden load changes there will be a short-time overshoot, and a special case is the instantaneous loss of load, load dump at full load. The usual specification states that the overshoot on load dump must not exceed 9 to 10 percent of rated speed. The settled speed rise will of course be equal to the regulation, 4 or 6 percent for a NEMA Class C or B governor and less than 1 percent for Class D.

Speed governors are classified as shown in Table 29-11.

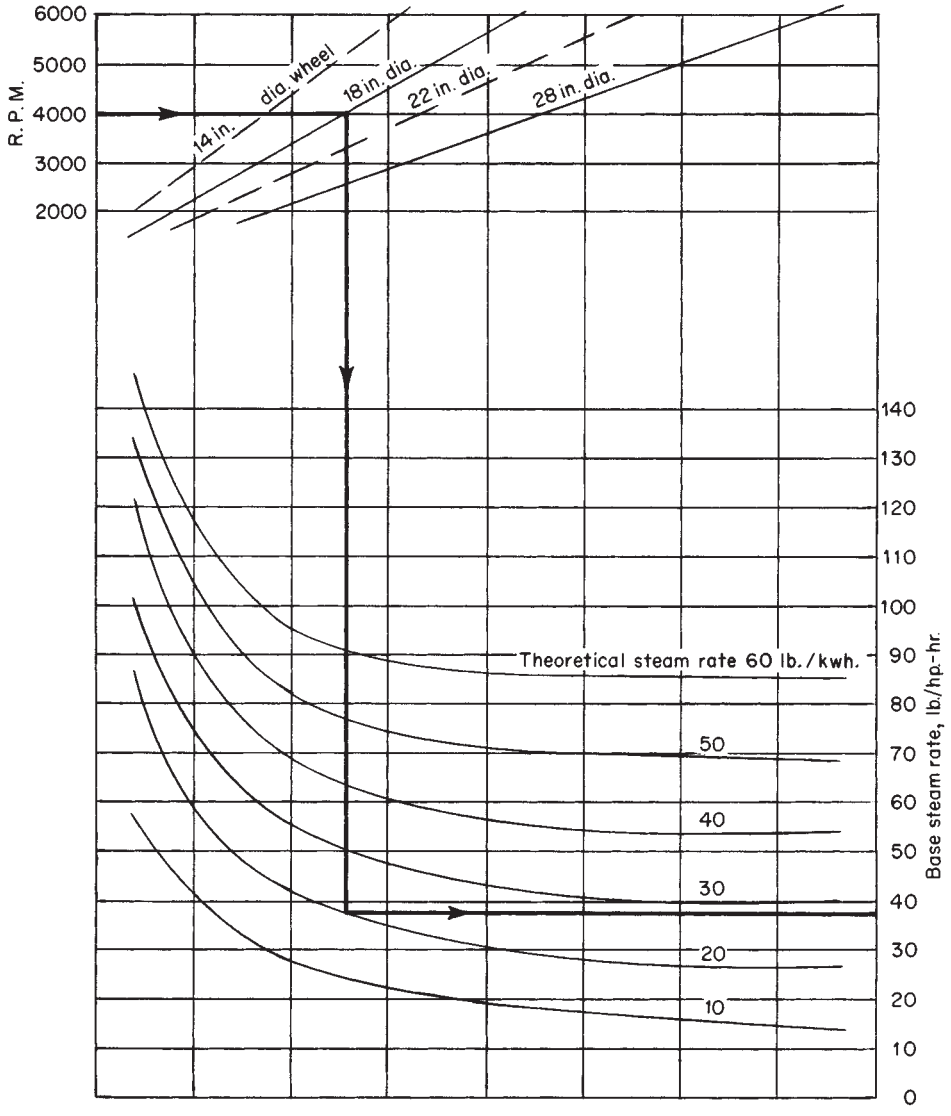


FIG. 29-15 Approximate steam rate for single-stage turbines. To convert pounds per kilowatthour to kilograms per kilowatthour, multiply by 0.4537; to convert inches to meters, multiply by 0.0254; and to convert pounds per horsepower-hour to kilograms per kilowatthour, multiply by 0.6084.

The **trip valve** is provided as a second line of defense in case of overspeed. The trip valve is frequently equipped with a trip-actuating solenoid which can be operated by push button, by low oil pressure, or by some other process upset. When the speed control functions as described above, the trip will not be actuated by load dump.

Extraction-Pressure Control An extraction turbine equipped with a regulator so that the extraction pressure will be automatically controlled is provided with two sets of steam-chest valves as shown in the schematic in Fig. 29-22. Each of the two sets of steam-chest valves is operated by a servomotor. The throttle flow is illustrated as the total of two flow streams: *A*, which travels the length of the turbine and leaves through the exhaust opening; and *B*, which leaves through the extraction opening. The shaft output is the sum of the power generated by the two streams. If the process demand increases, flow *B* increases and develops more power. For constant output, flow *A* must be reduced, and this is the function of the three-arm linkage: to open the governing valves and close the extraction valves, which will increase throttle flow ($A + B$) and decrease condenser flow *A* for more extraction flow at constant load. For a reduction the opposite happens.

For an increase or decrease in load the governor moves the three-arm link parallel to itself, and both sets of valves move in the same direction.

SELECTING A TURBINE

The **major variables** that affect turbine selection are as follows:

1. Horsepower and speed of the driven machine
2. Steam pressure and temperature available or to be decided
3. Steam needed for process, so that a back-pressure turbine should be considered
4. Steam cost and value of turbine efficiency, so that consideration can be given to stage and valve options
5. Use of speed-reducing or speed-increasing gears
6. Extraction for feedwater heating

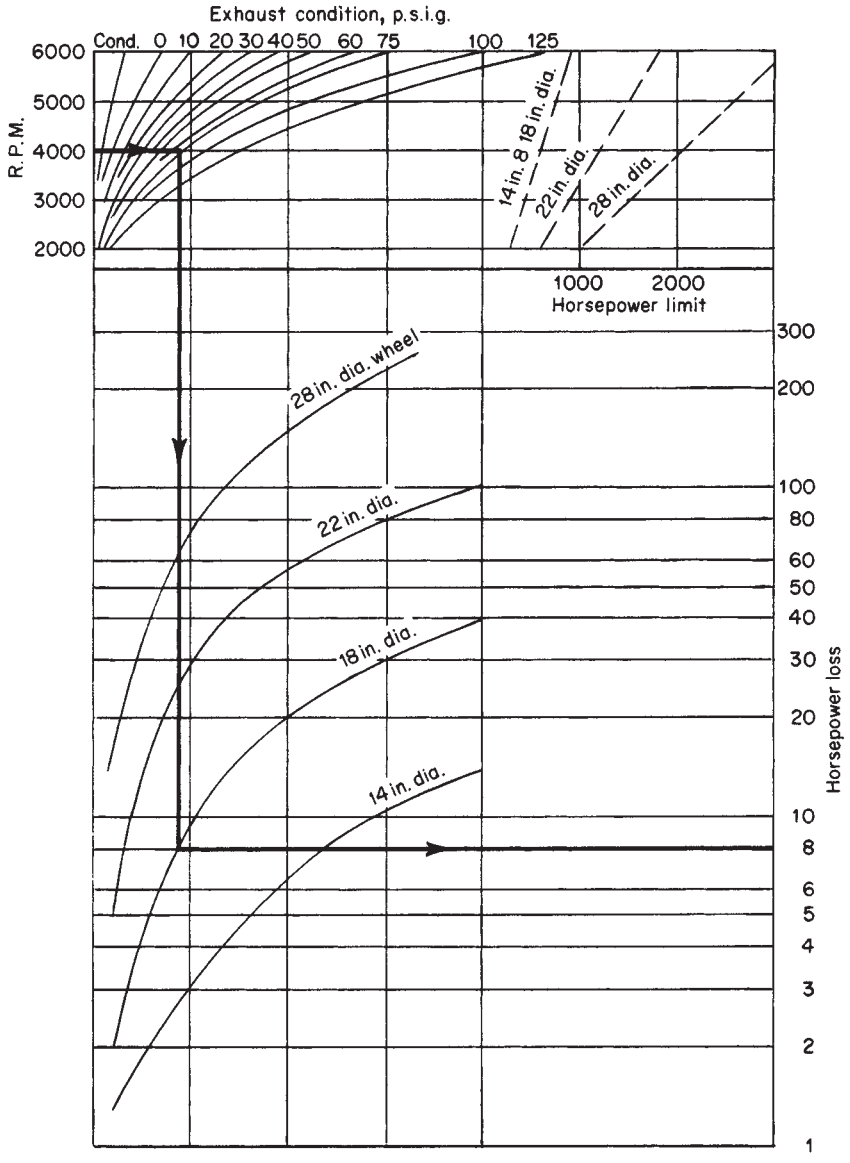


FIG. 29-16 Approximate horsepower loss for single-stage turbines. To convert horsepower to kilowatts, multiply by 0.7457; to convert inches to meters, multiply by 0.0254; and to convert pounds per square inch gauge to kilopascals, multiply by 6.895.

7. Condensing turbine with extraction for process
8. Control system, speed control, pressure control, and process control, so that consideration can be given to remote control, speed or pressure variation that can be tolerated, and system response speed
9. Safety features such as overspeed trip, low-oil trip, remote-solenoid trip, vibration monitor, or other special monitoring of temperature, temperature changes, and casing and rotor expansion
10. Price range from the minimum single-stage turbine to the most efficient multistage turbine

The **initial step in selection** could logically be to make an estimate of the steam flow at various steam pressures by using Fig. 29-17 for a rough estimate of efficiency. Unfortunately, there are no rigid standards for steam pressure and temperature as electrical-voltage steps are fixed, and many engineers pick a pressure and a temperature that look good to them. In general, however, manufacturers prefer working with the standards proposed by a joint ASME-IEEE committee. The values are 2760 kPa (400 psig) and 399° C (750° F), 4.140 kPa (600 psig) and 441° C (825° F), 5 860 kPa (850 psig) and 482° C (900° F), and 8.620 kpa (1250 psig) and 510° C (950° F) or 538° C (1000° F). The values fall on line *A* in Fig. 29-23. For a 1.5-inHg absolute exhaust pressure, line *A* corresponds to 9 percent moisture. Operating to the left of this state line (78 to 80 percent efficiency), last-stage moisture increases rapidly, which means more erosion; also less heat is available. Moving to the right of this line, the temperature lines become quite flat, the pressure drops at constant temperature, and heat available is reduced. It should be noted that 538° C (1000° F) is a good upper limit for steam turbines without a sharp increase in cost because of special materials. Experience has indicated that main-

TABLE 29-10 Typical Steam-Turbine Selection Table

Wheel diameter, in	Base steam rate, lb/hp·hr	Power loss, hp	Total power, hp	Steam required, lb/hr	Steam rate, lb/hp·hr
14	44.5	3.0	303	13,500	44.6
18	37.0	8.5	308.5	11,400	38.1
22	33.0	26.0	326.0	10,750	36.9
28	29.5	64.0	364.0	10,750	36.9

NOTE: To convert pounds per horsepower-hour to kilograms per kilowatthour, multiply by 0.6084; to convert horsepower to kilowatts, multiply by 0.7457.

tenance and initial cost exceed the gain in performance with temperatures in excess of the range of 538 to 566° C (1000 to 1050° F).

Example 1: Selection of Vacuum If a turbine is to be operated with exhaust to a condenser vacuum that will give 3 inHg absolute in the summer and 1 inHg absolute in the winter, what vacuum should be specified?

The turbine for 3 inHg will have shorter exhaust blades and a smaller exhaust opening and will lose 16 Btu/lb when operated at 1 inHg. It will also have a high pressure drop over the last-stage blading. Sonic velocity and shock waves will emanate from the last-stage blading, inducing blade loading and oscillation that may lead to fatigue failure. For operation at 1 inHg the last stage should operate with a diffuser which will limit the annulus discharge area of the stage. A turbine designed for 1 inHg will have a lot of windage in the last stage because the blade annulus cannot be filled by the higher-density steam.

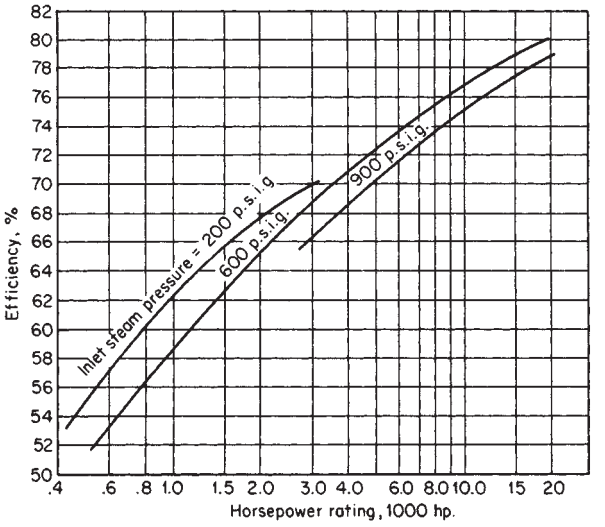


FIG. 29-17 Approximate efficiency for multistage turbines. To convert horsepower to kilowatts, multiply by 0.7457.

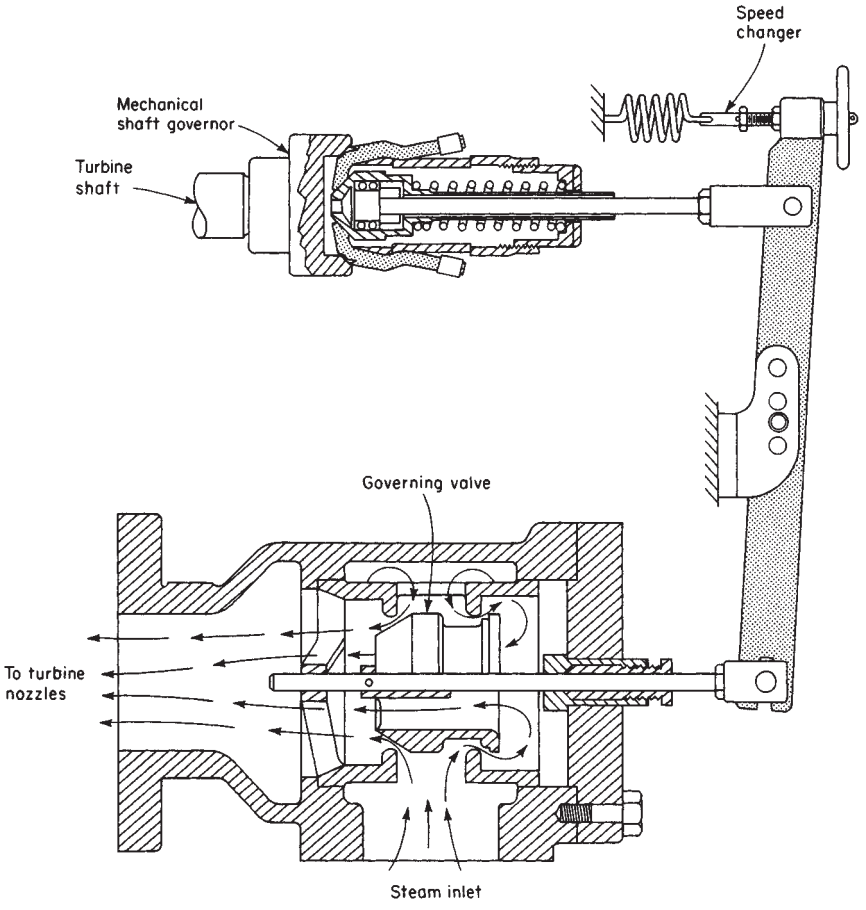


FIG. 29-18 Direct-acting flyball governor.

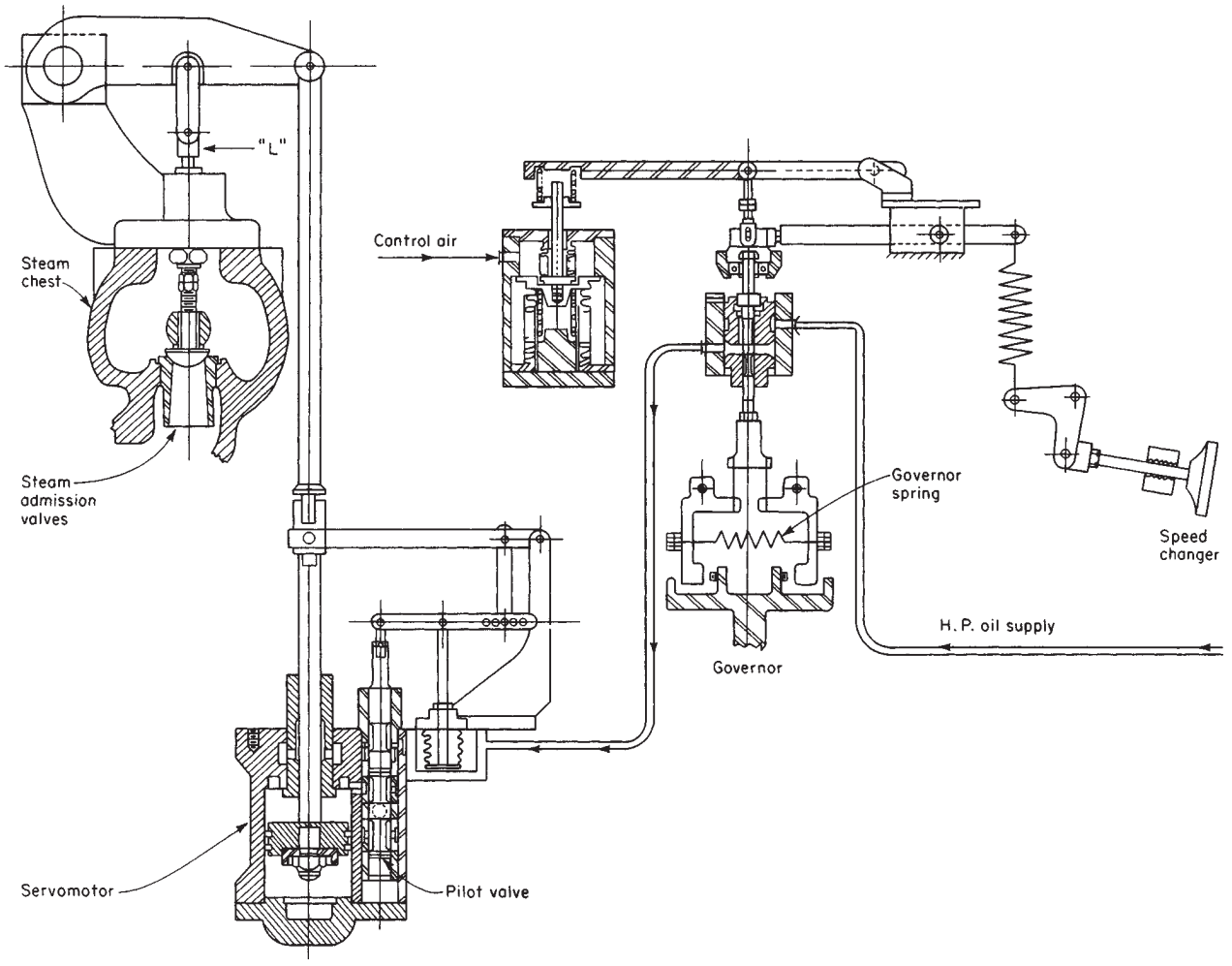


FIG. 29-19 Mechanical-hydraulic speed control: proportional.

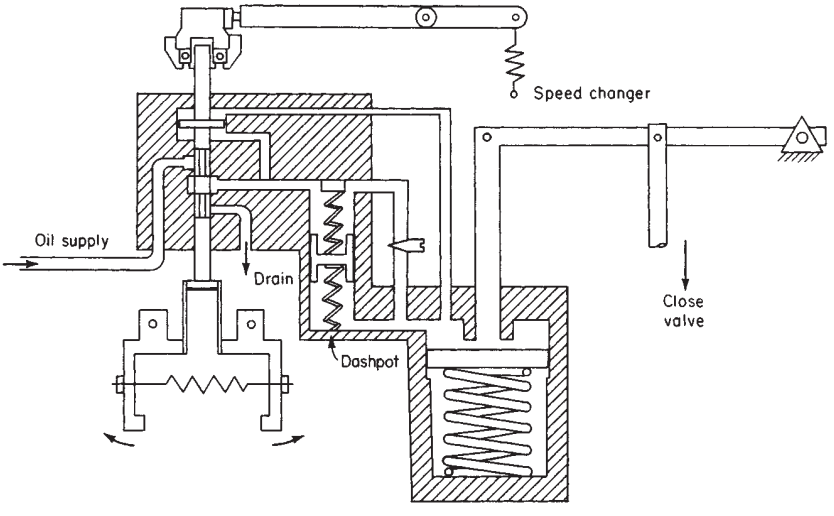


FIG. 29-20 Mechanical-hydraulic speed control: isochronous.

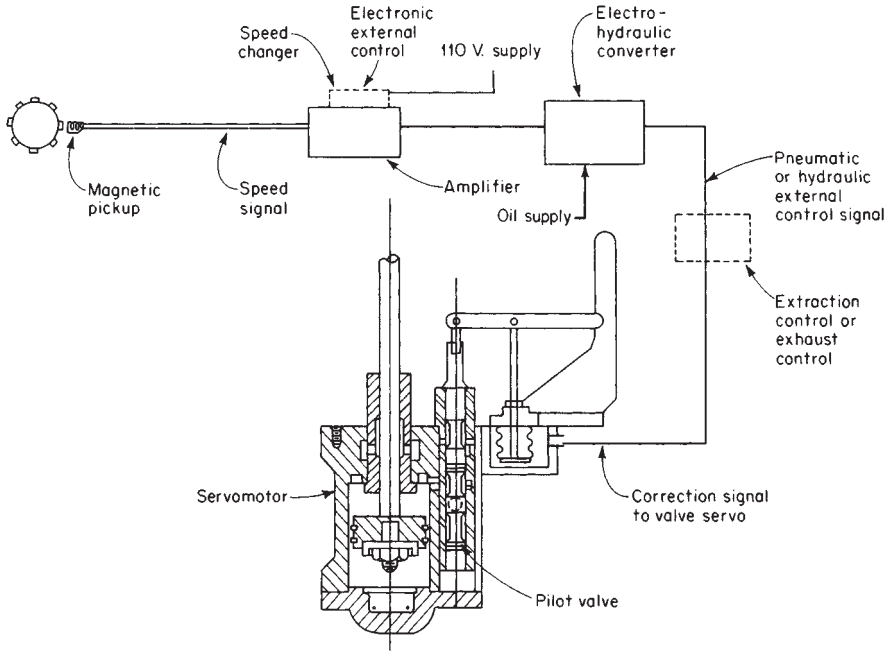


FIG. 29-21 Electrohydraulic speed control.

The best answer is an exhaust designed for 2 inHg and equipped with exhaust-blade diffuser. This will protect at 1 inHg and give some pressure recovery at 3 inHg by virtue of its venturi action.

When an **extraction-condensing turbine** is decided upon, it may be specified in three different ways, depending upon process steam and power demand. Referring to Fig. 29-24, the usual purchase is a unit in which rated capability can be carried either straight-condensing or total-extraction. The zero-extraction line terminates at *A*, and the total-extraction line terminates at *B*.

If the process-steam demand is high and steady, then the exhaust size can be reduced, because not much condensing capacity is required. The choice would be to save cost by a smaller exhaust which would terminate the zero-extraction line at *C*, while the total-extraction line would extend to *B* for rated capability.

TABLE 29-11 Classification of Speed Governors

Class of governor	Adjustable speed range	Maximum steady-state speed regulation	Maximum speed variables, plus or minus	Maximum speed rise	Trip speed (percent above rated speed)
A	10	10	0.75	13	15
	20	10	0.75	13	15
	30	10	0.75	13	15
	50	10	0.75	13	15
	65	10	0.75	13	15
B	10	6	0.50	7	10
	20	6	0.50	7	10
	30	6	0.50	7	10
	50	6	0.50	7	10
	65	6	0.50	7	10
	80	6	0.50	7	10
C	10	4	0.25	7	10
	20	4	0.25	7	10
	30	4	0.25	7	10
	50	4	0.25	7	10
	65	4	0.25	7	10
	80	4	0.25	7	10
D	30	0.50	0.25	7	10
	50	0.50	0.25	7	10
	65	0.50	0.25	7	10
	80	0.50	0.25	7	10
	85	0.50	0.25	7	10
	90	0.50	0.25	7	10

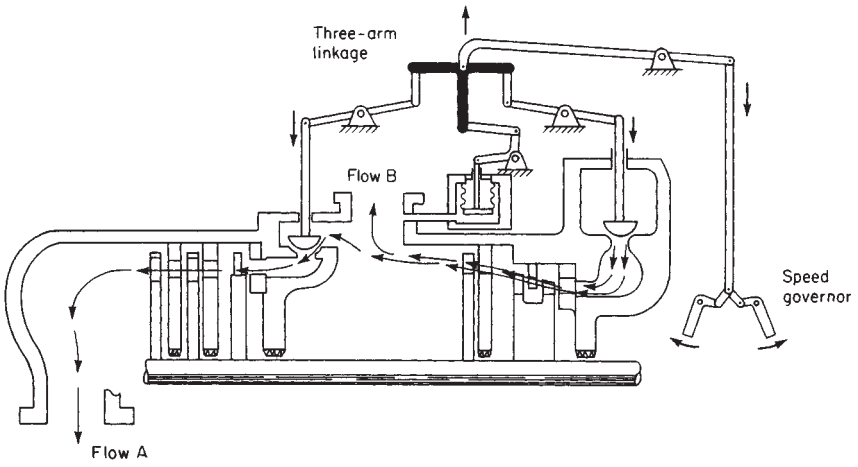


FIG. 29-22 Three-arm lever/mechanism for extraction-turbine-pressure control.

If the process demand is light and high-extraction flow is not required, then most of the power will be from the condensing flow. The choice would be to save cost by a smaller inlet and steam chest, which would terminate the total-extraction line at *D* and the zero-extraction line at *A*.

TEST AND MECHANICAL PERFORMANCE

When testing to establish the **thermodynamic performance** of a steam turbine, the ASME Performance Test Code 6 should be followed as closely as possible. The effect of deviations from code procedure should be carefully evaluated. The flow measurement is particularly critical, and Performance Test Code 19 gives details of flow nozzles and orifices. The test requirements should be carefully studied when the piping is designed to ensure that a meaningful test can be conducted.

Mechanical performance is generally checked by a running test at the factory before shipment and again when the turbine is installed on the site. The following is an enumeration of items that may provide smooth and vibration-free operation. The rotor must be in dynamic balance, and at-speed balancing is the most effective. The bearings must be in line, and the seal clearance must be correct. This alignment must be maintained when both cold and hot and during the transient from cold to hot. Disturbance of alignment may originate by unequal heat expansion of supports, from pipe expansion, or from binding and lack of freedom to expand. Excessive pipe expansion and high forces on the turbine have caused many vibration problems. Flexible couplings that do not flex also cause problems. This may result in torque lock or in unloading of bearings, and driver and driven machine bearings may be shifted out of line. Then there is the question of resonance and critical speed. The foundation enters into this relationship, and slender columns may contribute problems of resonance. If there is a gear in the lineup, it should be checked carefully for bearing load, alignment, and resonance frequencies that may be multiples of the gear ratio. Also, bearing-oil supply must be adequate.

From this it can be seen that **vibration** is the universal manifestation that something is wrong. Therefore, many units are equipped with instruments that continuously monitor vibration. Numerous new instruments for vibration analysis have become available. Frequency can be accurately determined and compared with computations, and by means of oscilloscopes the waveform and its harmonic components can be analyzed. Such equipment is a great help in diagnosing a source of trouble.

OPERATING PROBLEMS

While most turbines have a 10-year-availability record in the range of 95 to 99 percent, troubles may develop in any number of places. The most common are vibration, cycling governor, sticking valve stems, leaky packing, temperature bow, erosion of blading, loss of power, and bearing problems.

The causes of **vibration** have already been discussed. An increase in vibration over a period of time is generally caused by loss of alignment, settling of the foundation, or sticking of some expansion feature such as a pipe or a pedestal. Other causes are wear in the teeth of a flexible coupling, an internal rub in the unit, loss of bearing oil, and bearing wear. (Startup vibration is discussed later under temperature bow.)

If a **governor** starts to **cycle** after operating for some time, this is generally the result of wear which causes dead band or sticking. Also, all pilot valves should be inspected for the effects of dirt in the oil.

Sticking of valve stems is common if solids are present in the steam. The steam must be without solids. (Note comments later under loss of power.) It is important that units operating on a steady load for long periods be checked for sticking stems at regular intervals. The records show that in several cases deposits have caused the stem of both the governor valve and the trip valve to stick when there was a loss of load. The effect of the loss of load was destructive overspeed.

Wear and increased **leakage from the glands** are common. Carbon rings may need replacement after 1 or 2 years of operation. A unit with labyrinth packing may never need packing replacement. This depends upon operation. If a unit is started quickly with a temperature bow in the shaft, the result is a rub in the labyrinth, and then all packing may need replacement.

It is important to understand the reasons for a **temperature bow.** When a turbine is shut down and starts to cool, the lower half, particularly on a condensing unit, will cool faster than the top half. After the rotor has stopped turning, the temperature difference increases, and in 20 min there may be a 28 to 83° C (50 to 150° F) difference between top and bottom. Both the casing and the shaft bow up because of this temperature difference in the vertical plane. If the throttle is opened now and the bowed shaft starts to turn in the bowed casing, the packing may wipe out in a few revolutions, and at 200 r/min and up there will be a heavy thumping. The packing rub serves to increase the temperature bow by heating the high side of the shaft.

Other causes of a temperature bow are leaky valves and damaged sleeves. If steam is leaking into a stopped turbine from either an exhaust valve or a stop valve that is leaking, the upper half will be

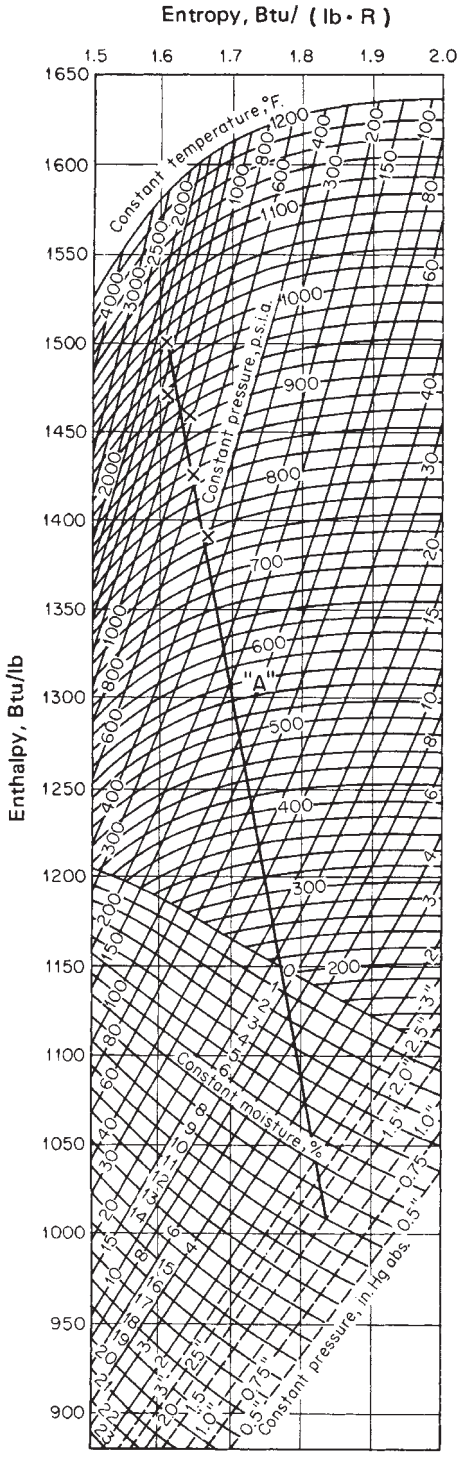


FIG. 29-23 Mollier diagram showing ASME-IEEE steam-turbine standards. To convert British thermal units per pound to kilojoules per kilogram, multiply by 2.328; to convert British thermal units per pound-degrees Rankine to joules per gram-Kelvin, multiply by 4.19; and to convert pounds-force per square inch to kilopascals, multiply by 6.89.

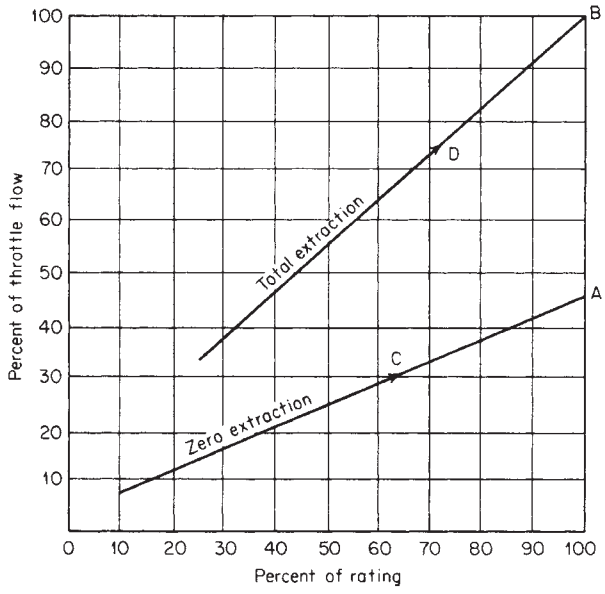


FIG. 29-24 Characteristic of extraction-condensing steam turbines.

warmer than the lower half, and it bows. If a shaft sleeve does not contact uniformly, there will be a transient difference in heat transfer to the shaft, and a bow will result. Also, turning sealing steam on before the shaft rotates may cause a bow.

Leaky valves are also a cause of **erosion.** Most turbine erosion-corrosion problems come from damage that takes place when the unit is not running. A slight steam leak into the turbine will let the steam condense inside the turbine, and salt from the boiler water will settle on the inside surfaces and cause pitting, even of the stainless blading. There must be two valves with a drain between them, i.e., a block valve on the header and an open drain in the line before it reaches the closed trip-throttle valve.

In a turbine that is running, erosion-corrosion is pretty much confined to units that are operating on saturated steam with inadequate boiler-water treatment. This type of erosion takes place behind the nozzle ring and around the diaphragms where they fit in the casing.

Loss of power is another item generally tied to water treatment. With dissolved salts in the steam these salts stay in solution while the steam is superheated. After the steam has expanded through several stages and become saturated, the salts condense out with the moisture. Silica and other salt deposits build up on the blading and the nozzles. The stage pressures increase, and the load drops. The thrust load increases, and the thrust bearing may fail. Depending upon the nature of the salts, it is possible to have corrosion associated with the deposits or corrosion only in the region where the steam changes from superheated to steam with moisture.

Turbine bearings show very little sign of wear as long as there is an adequate oil film. Wiping of the bearing is generally traced to dirt in the oil or a restriction in the oil supply. Thus filtration should be adequate and retain particles that may exceed the oil-film thickness. A checkerboard cracking of the babbitt is sometimes observed. This may have either of two origins. The shaft transports a lot of heat from the steam parts into the journal, and the oil flow in the bearing must be sufficient to lubricate and to remove this heat. Otherwise, the heat is conducted into the babbitt and the babbitt will soften and crack. This cracking may take place if oil flow is stopped too soon when a unit is shut down. The second origin for cracking of the bearing surface is pounding of the journal caused by shaft bow or oil whirl.

GAS TURBINES

The gas turbine is a power plant that produces a great amount of energy for its size and weight. The gas turbine has found increasing service in the past 15 years in the petrochemical industry and utilities throughout the world. It is the power source of the aircraft industry. In this section we deal with land-based gas turbines.

The gas turbine in a combined cycle mode will be the power source through the year 2020 for most countries throughout the world. Most of the new power plants of the 1990s are and will continue to be run by gas turbines with steam turbines in a combined cycle mode. Its compactness, low weight, and multiple fuel application also make it a natural power plant for offshore platforms. Today there are gas turbines that run on natural gas, diesel fuel, naphtha, methane, crude, low-Btu gases, vaporized fuel oils, and even waste. In the 1950s and 1960s, the gas turbine was perceived as a relatively inefficient power source when compared to other power sources. Its efficiencies, compactness, and light weight made it attractive for certain applications. The limiting factor for most gas turbines has been the turbine inlet temperature. With new schemes of air cooling and breakthroughs in blade metallurgy, higher turbine temperatures have been achieved.

The new gas turbines have fired inlet temperatures as high as 2300° F (1260° C) with efficiencies as high as 42–45 percent. Pressure ratios have increased from 5:1 in the 1950s to as high as 30:1 in some of the new turbines of the 1990s. Gas turbines are classified into two major categories:

1. Industrial heavy-duty gas turbines
2. Aeroderivative gas turbines

INDUSTRIAL HEAVY-DUTY GAS TURBINES

The gas turbine was designed shortly after World War II and introduced to the market in the early 1950s. The early heavy-duty gas turbine design was largely an extension of steam turbine design. Restrictions of weight and space were not important factors for these ground-based units, so the design characteristics included heavy-wall casings split on horizontal centerlines, hydrodynamic (tilting pad) bearings, large-diameter combustors, thick airfoil sections for blades and stators, and large frontal areas. The overall pressure ratio of these units varied from 5:1 for the earlier units to 30:1 for the units in the 1990s. Turbine inlet temperatures have been increased and run as high as 2300° F (1260° C) on some of these units. Projected temperatures approach 3000° F (1649° C) and, if achieved, would make the gas turbine even more efficient. The industrial heavy-duty gas turbines most widely used employ axial-flow compressors and turbines. In most U.S. designs combustors are can-annular combustors. Single-stage side combustors are used in European designs. The combustors used in industrial gas turbines have heavy walls and are very durable.

AERODERIVATIVE GAS TURBINES

The aeroderivative gas turbine, as its name implies, is composed of an aeroengine that produces high temperature and high pressure gas that is then put through a power turbine to produce the energy required. The aeroengine is the gas generator. It is usually an engine developed for an aircraft that is modified by the addition of compression stages to produce the high pressure and high temperature required. The gas generator serves to raise combustion gas products for the power turbine to a pressure of about 45–75 psig (3–5 Bar) and temperatures between 900° F (482° C) and 1200° F (649° C). The gas generator is very lightweight compared to the industrial gas turbine. The gas generator is characterized by light casing walls, blades with high aspect ratio (blade length/blade chord), roller bearings, annular combustors, and light weight.

The power turbine is free (i.e., the power turbine is not physically coupled to the gas generator but is closely coupled to the gas generator by a transition duct that transports the gas from the gas generator to the power turbine). The power turbine is an industrial-type turbine in design characterized by heavy wall casings, hydrodynamic (tilting pad) bearings, and thick airfoil sections. The rotative power produced in the gas turbine is then available for mechanical coupling to the driven equipment.

MAJOR GAS TURBINE COMPONENTS

The gas turbine in the simple cycle mode consists of a compressor (axial or centrifugal) that compresses the air, a combustor that heats the air at constant pressure and a turbine that expands the high pressure and high temperature combustion gases and produces power to run the compressor and through a mechanical coupling to the driven equipment. The power required to compress the gases varies from about 40–60 percent of the total power produced by the turbine.

Compressors A compressor is a device that pressurizes the air in a gas turbine. It transfers energy by dynamic means from a rotating member to the continuously flowing air. The two types of compressors used in gas turbines are axial and centrifugal. Figures 29-25 and 29-26 depict typical industrial gas turbines.

The axial flow compressor is used in over 95 percent of the gas turbines. An axial-flow compressor in a gas turbine compresses the working air by first accelerating the air and then diffusing it to obtain a pressure increase. The air is accelerated by a row of rotating airfoils or blades (the rotor) and diffused by a row of stationary blades (the stator). The diffusion in the stator converts the velocity increase gained in the rotor to a pressure increase. One rotor and one stator make up a stage in a compressor. A compressor usually consists of several stages: a typical compressor contains about 15–17 stages. One additional row of fixed blades (inlet guide vanes) is frequently used at the compressor inlet to ensure that air enters the first-stage blading at the desired angle. In addition to the stators, an additional diffuser at the exit of the compressor further diffuses the air and controls its velocity when entering the combustors.

In an axial compressor air passes from one stage to the next with each stage raising the pressure slightly. By producing low pressure increases on the order of 1.1:1 to 1.4:1, very high efficiencies (85–90 percent) can be obtained. The use of multiple stages permits overall pressure increases up to 30:1. The axial-flow compressor has a very narrow operating range. The operating range is defined as the range between surge and choke. *Surge* is when the flow in a compressor reverses itself; this phenomenon is very destructive. *Choke,* sometimes called "stone wall," is the point where the compressor flow has reached a maximum; this is accomplished by great loss in efficiency.

In the centrifugal or mixed-flow compressor, the air enters the compressor in an axial direction and exits in a radial direction into a diffuser. This combination of rotor (or impeller) and diffuser comprises a single stage. The air initially enters a centrifugal compressor at the inducer. The inducer, usually an integral part of the impeller, is very much like an axial-flow compressor rotor. Many European designs keep the inducer separate. The air then goes through a 90° turn and exits into a diffuser, which usually consists of a vaneless space followed by a vaned diffuser.

From the exit of the diffuser, the air enters a scroll or collector. The pressure ratio per stage in a centrifugal compressor can vary from about 1.5:1 to 9:1 on production units. Some experimental units have obtained pressure ratios of more than 12:1 for a single stage. The centrifugal compressor is slightly less efficient (78–83 percent) than the axial-flow compressor but has a higher stability. A higher stability means that its operating range (surge-to-choke margin) is greater; however, like the axial-flow unit, this range is reduced as the pressure ratio is increased.

Regenerators Regenerators are used in gas turbines to increase the turbine efficiency. They are placed between the compressor and the combustor. Heavy-duty regenerators are designed for applications in large gas turbines in the 5000–100,000-hp range. The use of regenerators in conjunction with industrial gas turbines substantially increases cycle efficiency and provides an impetus to energy management by reducing fuel consumption up to 30 percent. In most present-day regenerative gas turbines, ambient air enters the inlet fil-

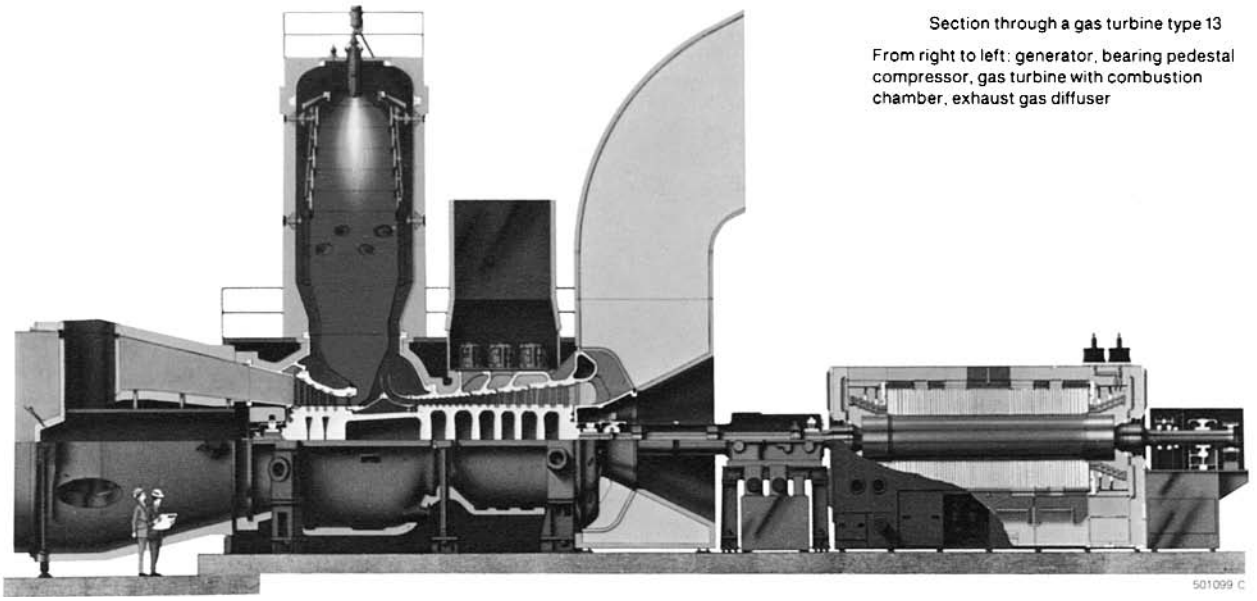
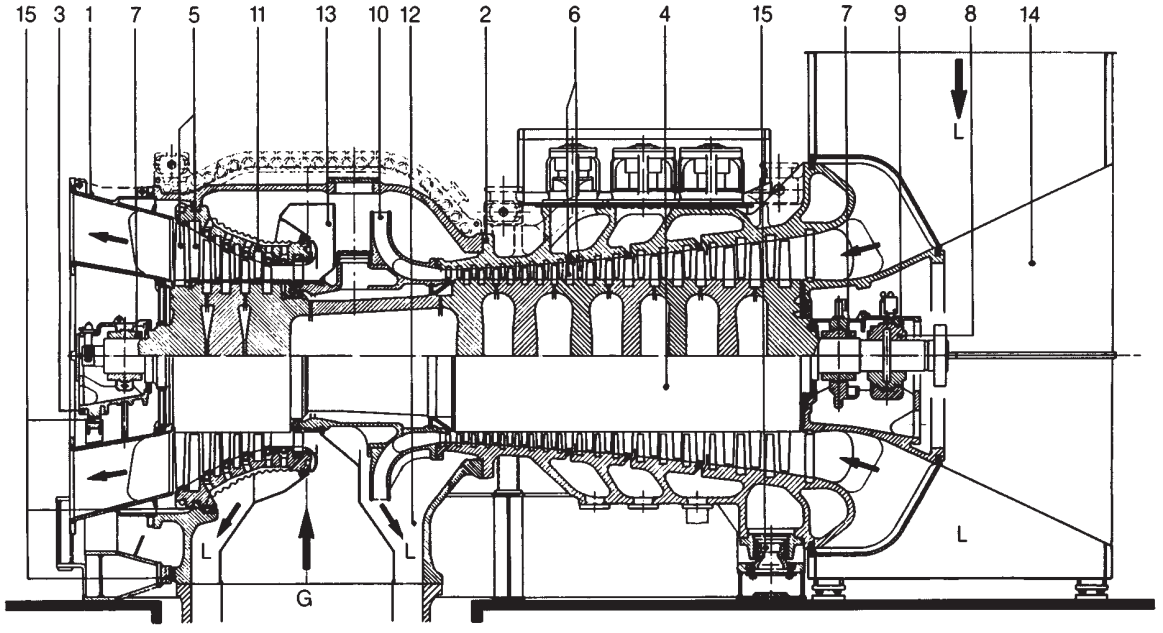


FIG. 29-25 Section through a Brown-Boveri gas turbine (with permission of Asea-Brown Boveri).



1 = Turbine housing
2 = Compressor housing
3 = Bearing body
4 = Shaft
5 = Turbine rotor and stator blades
6 = Compressor rotor and stator blades
7 = Journal bearings
8 = Thrust bearings
9 = Thrust bearing cover
10 = Diffuser
11 = Blade carrier
12 = Cooling-air admission
13 = Internal casing
14 = Air intake
15 = Position key

L = Air
G = Hot gas

FIG. 29-26 Principal components of a Brown-Boveri gas turbine (with permission of Asea-Brown Boveri).

ter and is compressed. The air is then piped to the regenerator, which heats the air to about 900° F (482° C). The heated air then enters the combustor, where it is further heated before entering the turbine. After the gas has undergone expansion in the turbine, it is about 1000° F (538° C)–1100° F (593° C) and essentially at ambient pressure. The gas is ducted through the regenerator where the waste heat is transferred to the incoming air. The gas is then discharged into the ambient air through the exhaust stack. In effect, the heat that would otherwise be lost is transferred to the air, decreasing the amount of fuel that must be consumed to operate the turbine. For a 30,000-hp turbine, the regenerator heats 10 million pounds (453,000 kg) of air per day.

Combustors All gas turbine combustors perform the same function: They increase the temperature of the high-pressure gas at constant pressure. The gas turbine combustor uses very little of its air (10 percent) in the combustion process. The rest of the air is used for cooling and mixing. The air from the compressor must be diffused before it enters the combustor. The velocity leaving the compressor is about 400–500 ft/sec (130–164 m/sec), and the velocity in the combustor must be maintained at about 10–30 ft/sec (3–10 m/sec). Even at these low velocities, care must be taken to avoid the flame to be carried downstream. To ensure this, a baffle creates an eddy region that stabilizes the flame and produces continuous ignition. The loss of pressure in a combustor is a major problem, since it affects both the fuel consumption and power output. Total pressure loss is in the range of 2–8 percent; this loss is the same as the decrease in compressor efficiency.

Despite the many design differences, all gas turbine combustion chambers have three features: (1) a recirculation zone, (2) a burning zone with a recirculation zone that extends to the dilution region, and (3) a dilution zone. The function of the recirculation zone is to evaporate, burn in part, and prepare the fuel for rapid combustion within the remainder of the burning zone. Ideally, at the end of the burning zone, all fuel should be burnt so that the function of the dilution zone is solely to mix the hot gas with the dilution air. The mixture leaving the chamber should have a temperature and velocity distribution acceptable to the turbine nozzles. Generally, the addition of dilution air is so abrupt that if combustion is not complete at the end of the burning zone, chilling occurs, which prevents completion. However, there is evidence with some chambers that if the burning zone is run overrich, some combustion does occur within the dilution region. Combustor inlet temperature depends on engine pressure ratio, load and engine type, and whether the turbine is regenerative or nonregenerative. Nonregenerative inlet temperatures vary from 250° F (121° C) to 1000° F (593° C), while regenerative inlet temperatures range from 700° F (371° C) to 1200° F (649° C). Combustor outlet temperatures range from 1500° (815° C) to 3000° F (1649° C) for large turbines. Combustor pressures for a full-load operation vary from 45 psia (310 kPa) for small engines to as much as 450 psia (3100 kPa) in complex engines. Fuel rates vary with load, and fuel atomizers may be required for flow ranges as great as 100:1. However, the variation in the fuel-to-air ratio between idle and full-load conditions usually does not vary. At lightoff and during acceleration, a much higher fuel-to-air ratio is needed because of the higher temperature rise. On deceleration, the conditions may be appreciably leaner. Thus, a combustor that can operate over a wide range of mixtures without danger of blowouts simplifies the control system.

Combustor performance is measured by efficiency, the pressure decrease encountered in the combustor, and the evenness of the outlet temperature profile. Combustion efficiency is a measure of combustion completeness. Combustion completeness affects fuel consumption directly, since the heating value of any unburned fuel is not used to increase the turbine inlet temperature. The uniformity of the combustor outlet profile affects the useful level of turbine inlet temperature, since the average gas temperature is limited by the peak gas temperature. This uniformity assures adequate nozzle life, which depends on operating temperature. The average inlet temperature to the turbine affects both fuel consumption and power output. A large combustor outlet gradient will work to reduce average gas temperature and consequently reduce power output and efficiency. Combustors in a gas turbine can be arranged in many different ways. These arrangements can be classified into three main categories:

1. Tubular (side combustors)
2. Can-annular combustors
3. Annular combustors

Tubular (Side Combustors) Tubular or single-can designs are preferred by many European industrial gas turbine designers. These large single combustors offer the advantage of simplicity of design and long life because of low heat-release rates. These combustors are sometimes very large. They can range in size from small units of about 6 inches (152 mm) in diameter to 1-foot (300-mm) combustors that are over 10 feet (3 m) in diameter and 30–40 feet (10–13 m) high. These large combustors use special tiles as liners. Any liner damage can be easily corrected by replacing the damaged tiles. The tubular combustors can be designed as "straight-through" or "reverse-flow" designs. Most large single-can combustors are of the reverse-flow design. In this design, the air enters the turbine through the annulus between the combustor can and the hot gas pipe. The air then passes between the liner and the combustor can and enters the combustion region at various points of entry. About 10 percent of the air enters the combustion zone, about 30–40 percent of the air is used for cooling purposes, and the rest is used in the dilution zone. Reverse-flow designs reduce the combustor lengths as compared to the straight-through flow designs.

Larger tubular, or single-can, units usually have more than one nozzle. In many cases a ring of nozzles is placed in the primary zone area. The radial and circumferential distribution of the temperature to the turbine nozzles is not as even as in tubo-annular combustors. In some cases, high stresses are exerted on the turbine casing leading to casing cracks.

Can-Annular Combustors Can-annular combustors are the most common type of combustors used in gas turbines. The industrial gas turbines designed by U.S. companies use the tubo-annular or can-annular type. The advantage to these types of combustors is the ease of maintenance. They also have a better temperature distribution than the side single-can combustor and can be of the straight-through or reverse-flow design. As with the single-can combustor, most of these combustors are of the reverse-flow design in industrial turbines.

In most aircraft engines, the can-annular combustors are of the straight-through flow type. The straight-through flow-type tubo-annular combustor requires a much smaller frontal area than the reverse-flow-type can-annular combustor. The can-annular combustor also requires more cooling air flow than a single or annular combustor because the surface area of the can-annular combustor is much greater. The amount of cooling air is not much of a problem in turbines using high-Btu gas, but for low-Btu gas turbines, the amount of air required in the primary zone is increased from 10 percent to as high as 35 percent of the total air, thus reducing the amount of air available for cooling purposes.

Higher temperatures also require more cooling and, as temperatures increase, the single can or annular combustor design becomes more attractive. The tubo-annular combustor has a more even combustion because each can has its own nozzle and a smaller combustion zone, resulting in a much more even flow. Development of a can-annular combustor is usually less expensive, since only one needs to be tested instead of an entire unit as in an annular or single-can combustor. Therefore, the fuel and air requirements can be as low as 8–10% of the total requirements.

Annular Combustors Annular combustors are used mainly in aircraft-type gas turbines where frontal area is important. There are smaller sized industrial turbines that also have annular combustors. This type of combustor is usually a straight-through flow type. The combustor outside radius is the same as the compressor casing, thus producing a streamline design. The annular combustor mentioned earlier requires less cooling air than the tubo-annular combustor, so it is growing in importance for high-temperature applications. On the other hand, the annular combustor is much harder to get to for maintenance and tends to produce a less favorable radial and circumferential profile as compared to the can-annular combustors. The annular combustors are also used in some newer industrial gas turbine applications. The higher temperatures and low-Btu gases will foster more use of annular-type combustors in the future.

Turbines The two types of turbine geometries used in gas turbines are the axial-flow and the radial-inflow type. The axial-flow

turbine is used in more than 95 percent of all applications in a gas turbine.

Radial-Inflow Turbine The radial-inflow turbine, or inward-flow radial turbine, has been in use for many years. Basically a centrifugal compressor with reversed-flow and opposite rotation, the inward-flow radial turbine is used for smaller loads and over a smaller operational range than the axial turbine. Radial-inflow turbines are only now beginning to be used because little was know about them heretofore. Axial turbines have enjoyed tremendous interest due to their low frontal area, making them suited to the aircraft industry. However, the axial machine is much longer than the radial machine, making it unsuited for certain vehicular and helicopter applications. Radial turbines are used in turbochargers and in some types of expanders.

The inward-flow radial turbine has many components similar to a centrifugal compressor. The mixed-flow turbine is almost identical to a centrifugal compressor—except its components have different functions. The scroll is used to distribute the gas uniformly around the periphery of the turbine. The nozzles, used to accelerate the flow toward the impeller tip, are usually straight vanes with no airfoil design. The vortex is a vaneless space and allows an equalization of the pressures. The flow enters the rotor radially at the tip with no appreciable axial velocity and exits the rotor through the exducer axially with little radial velocity. These turbines are used because of lower production costs, in part because the nozzle blading does not require any camber or airfoil design. They are also more robust, but due to cooling restrictions are used for much lower turbine inlet temperatures.

Axial-Flow Turbine The axial-flow turbine is very widely used in gas turbines (95 percent). These axial flow turbines, like their counterparts, the axial-flow compressors, have flow that enters and leaves in an axial direction. Axial-flow turbines are the most widely employed turbines using a compressible fluid. Axial-flow turbines power most gas turbine units—except the smaller horsepower turbines—and they are more efficient than radial-inflow turbines in most operational ranges. Axial-flow turbine efficiencies range from 88–92 percent. The axial-flow turbine is also used in steam turbine design; however, there are some significant differences between the axial-flow turbine design for a gas turbine and the design for a steam turbine. Steam turbine development preceded the gas turbine by many years. Thus, the axial-flow turbine used in gas turbines is an outgrowth of steam turbine technology. In recent years, the trend towards high turbine inlet temperatures in gas turbines has required various cooling schemes and improved materials.

There are two types of axial turbines:

1. Impulse type
2. Reaction type

An impulse-type turbine experiences its entire enthalpy drop in the nozzle, thus having a very high velocity entering the rotor. The velocity entering the rotor is about twice the velocity of the wheel. The reaction type turbine divides the enthalpy drop in the nozzle and in the rotor. Thus, for example, a 50 percent reaction turbine has a velocity leaving the nozzle equal to the wheel speed and produces about ½ the work of a similar size impulse turbine at about 2–3 percentage points higher efficiency than the impulse turbine (0 percent reaction turbine). The effect on the efficiency and ratio of the wheel speed to inlet velocity is shown in Fig. 29-27 for an impulse turbine and 50 percent reaction turbine.

Impulse Turbine The impulse turbine is the simplest type of turbine. It consists of a group of nozzles followed by a row of blades. The gas is expanded in the nozzle, converting the high thermal energy into kinetic energy. This conversion can be represented by the following relationship:

$$V = \sqrt{2\Delta h} \tag{29-15}$$

The high-velocity gas impinges on the blade where a large portion of the kinetic energy of the moving gas stream is converted into turbine shaft work. Figure 29-28 shows a diagram of a single-stage impulse turbine. The static pressure decreases in the nozzle with a corresponding increase in the absolute velocity. The absolute velocity is then reduced in the rotor, but the static pressure and the relative velocity remain constant. To get the maximum energy transfer, the blades must rotate at about one-half the velocity of the gas jet velocity. By definition, the impulse turbine has a degree of reaction equal to zero. This degree of reaction means that the entire enthalpy drop is taken in the nozzle, and the exit velocity from the nozzle is very high. Since there is no change in enthalpy in the rotor, the relative velocity entering the rotor equals the relative velocity exiting from the rotor blade. For the maximum utilization, the absolute exit velocity must be axial.

The Reaction Turbine The axial-flow reaction turbine is the most widely used turbine. In a reaction turbine, both the nozzles and blades act as expanding nozzles. Therefore, the static pressure decreases in both the fixed and moving blades. The fixed blades act as nozzles and direct the flow to the moving blades at a velocity slightly higher than the moving-blade velocity. In the reaction turbine, the velocities are usually much lower, and the entering blade relative velocities are nearly axial. Figure 29-29 shows a schematic view of a reaction turbine. In most designs, the reaction of the turbine blade varies from hub to shroud. The impulse turbine is a reaction turbine with a reaction of zero ($R = 0$). The utilization factor that is a ratio of the ideal work to the energy supplied for a fixed nozzle angle will increase as the reaction approaches 100 percent. For $R = 1$, the utilization factor does not reach

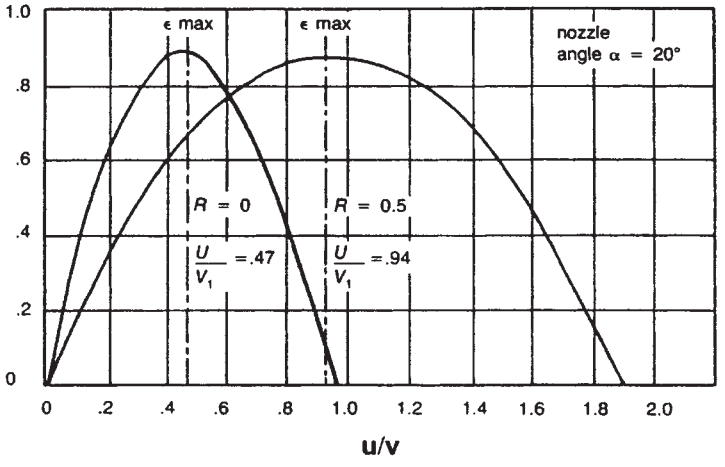


FIG. 29-27 Variation of utilization factor with U/V_1 for $R = 0$ and $R = 0.5$. (*From* Principles of Turbomachinery *by Dennis G. Shepherd, Copyright 1956 by Macmillan Publishing Co., Inc.*)

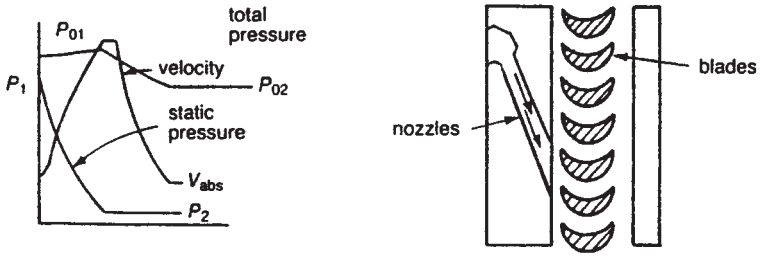


FIG. 29-28 View of a single-stage impulse turbine with velocity and pressure distribution.

unity but reaches some maximum finite value. The 100 percent reaction turbine is not practical because of the high rotor speed necessary for a good utilization factor. For reaction less than zero, the rotor has a diffusing action. Diffusing action in the rotor is undesirable, since it leads to flow losses. The 50 percent reaction turbine has been used widely and has special significance. The velocity diagram for a 50 percent reaction is symmetrical and, for the maximum utilization factor, the exit velocity must be axial. The pressure and velocity distributions in a reaction-type turbine are also shown in Fig. 29-29.

The work produced in an impulse turbine with a single stage running at the same blade speed is twice that of a reaction turbine. Hence, the cost of a reaction turbine for the same amount of work is much higher, since it requires more stages. It is a common practice to design multistage turbines with impulse stages in the first few stages to maximize the work and pressure decrease and to follow it with 50 percent reaction turbines. The reaction turbine has a higher efficiency due to blade suction effects. This type of combination leads to an excellent compromise, since otherwise an all-impulse turbine would have a low efficiency, and an all-reaction turbine would have many more stages.

Turbine-Blade Cooling The turbine inlet temperatures of gas turbines have increased considerably over the past years and will continue to do so. This trend has been made possible by advancement in materials and technology, and the use of advanced turbine blade-cooling techniques. The blade metal temperature must be kept below 1400° F (760° C) to avoid hot corrosion problems. To achieve this cooling air is bled from the compressor and is directed to the stator, the rotor, and other parts of the turbine rotor and casing to provide adequate cooling. The effect of the coolant on the aerodynamic, and thermodynamics depends on the type of cooling involved, the temperature of the coolant compared to the mainstream temperature, the location and direction of coolant injection, and the amount of coolant.

In high-temperature gas turbines, cooling systems need to be designed for turbine blades, vanes, endwalls, shroud, and other components to meet metal temperature limits. Figure 29-30 shows the various types of air-cooling schemes used. The concepts underlying the following five basic air-cooling schemes are:

1. Convection cooling
2. Impingement cooling
3. Film cooling
4. Transpiration cooling
5. Water cooling

Until the late 1960s, convection cooling was the primary means of cooling gas turbine blades; some film cooling was occasionally employed in critical regions. However, in the early 1970s, other advanced cooling schemes were considered due to the greater cooling requirements for engines under development, and in the 1990s, these cooling schemes have been implemented. It should be noted that if more than 6–8 percent of the air is used in cooling, then the effect of the higher temperature becomes negated.

Convection Cooling This form of cooling is achieved by designing the cooling air to flow inside the turbine blade or vane and remove heat through the walls. Usually, the air flow is radial, making multiple passes through a serpentine passage from the hub to the blade tip. Convection cooling is the most widely used cooling concept in present-day gas turbines.

Impingement Cooling In this high-intensity form of convection cooling, the cooling air is blasted on the inner surface of the airfoil by high-velocity air jets, permitting an increased amount of heat to be transferred to the cooling air from the metal surface. This cooling method can be restricted to desired sections of the airfoil to maintain even temperatures over the entire surface. For instance, the leading edge of a blade needs to be cooled more than the midchord section or trailing edge, so the gas is impinged on that surface.

Film Cooling This type of cooling is achieved by allowing the working air to form an insulating layer between the hot gas stream and the walls of the blade. This film of cooling air protects an airfoil in the same way combustor liners are protected from hot gases at very high temperatures.

Transpiration Cooling Cooling by this method requires the coolant flow to pass through the porous wall of the blade material. The heat transfer is directly between the coolant and the hot gas. Transpiration cooling is effective at very high temperatures, since it covers the entire blade with coolant flow. This method has been used rarely due to high costs.

Water Cooling Water is passed through a number of tubes embedded in the blade. The water is emitted from the blade tips as steam to provide excellent cooling. This method keeps blade metal temperatures below 1000° F (538° C); however, a full application of this method is not expected until the year 2000.

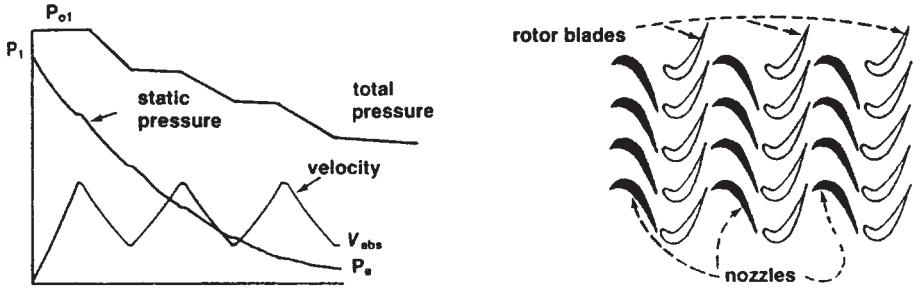


FIG. 29-29 Velocity and pressure distribution in a three-stage reaction turbine.

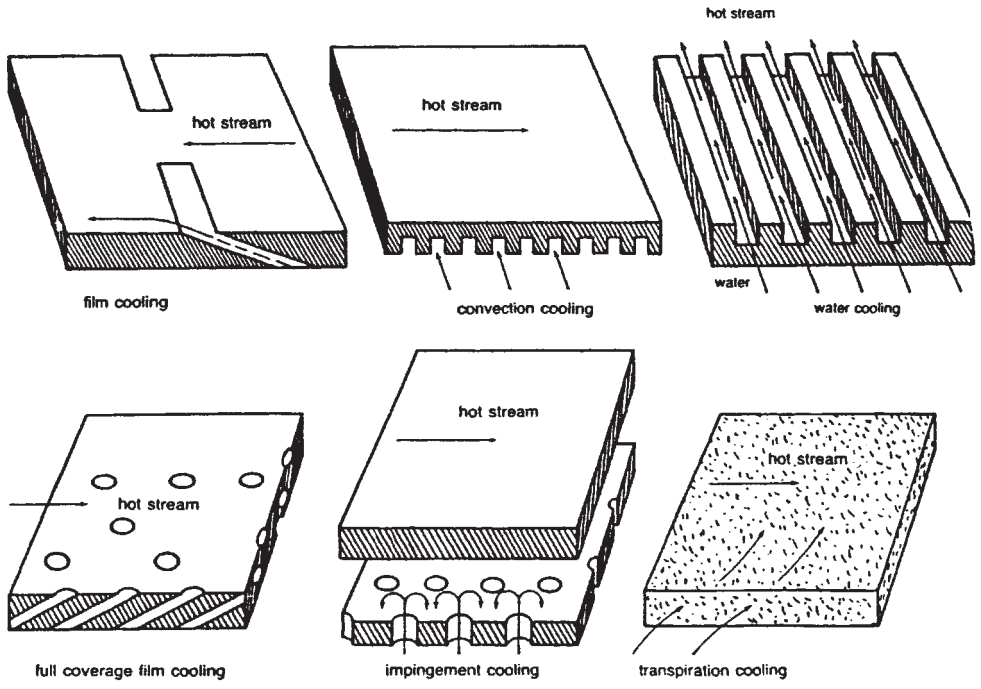


FIG. 29-30 Various suggested cooling schemes.

The incorporation of the above blade cooling concepts into actual blade designs is very important. The most frequently used blade cooling designs are:

1. Convection and impingement cooling
2. Film and convection cooling

It should be noted that in a blade the highest temperatures are encountered at the trailing edge and the highest stress points at about ⅓ the height from the base at the trailing edge.

Convection and Impingement Cooling Strut Insert Design The strut insert design has a midchord section that is convection-cooled through horizontal fins, and a leading edge that is impingement cooled. The coolant is discharged through a split trailing edge.

The air flow up the central cavity formed by the strut insert and through holes at the leading edge of the insert to impingement cool the blade leading edge. The air then circulates through horizontal fins between the shell and strut and discharges through slots in the trailing edge. The temperature distribution for this design is shown in Fig. 29-31. The stresses in the strut insert are higher than those in the shell, and the stresses on the pressure side of the shell are higher than those on the suction side. Considerably more creep strain takes place toward the trailing edge than the leading edge. The creep strain distribution at the hub section is unbalanced. This unbalance can be improved by a more uniform wall temperature distribution.

Film and Convection Cooling Design This type of blade design has a midchord region that is convection cooled, and the leading edges which are both convection and film cooled. The cooling air is injected through the blade base into two central and one leading edge cavity. The air then circulates up and down a series of vertical passages. At the leading edge, the air passes through a series of small holes in the wall of the adjacent vertical passages and then impinges on the inside surface of the leading edge and passes through film-cooling holes. The trailing edge is convection cooled by air discharging through slots.

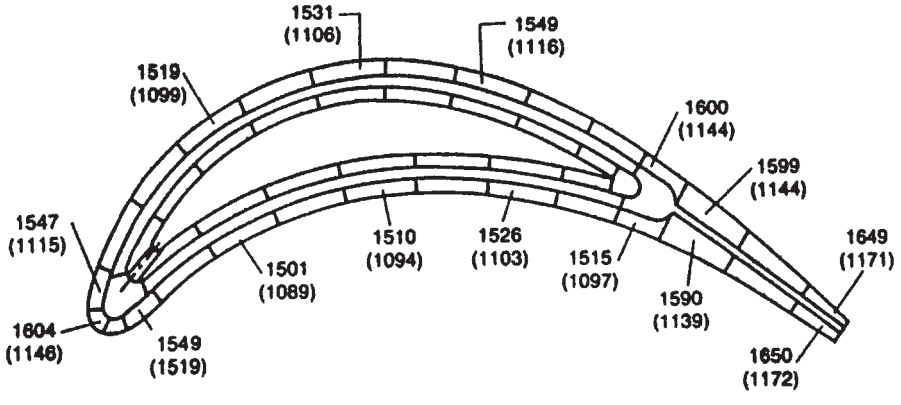


FIG. 29-31 Temperature distribution for strut insert design, °F (cooled).

The temperature distributions for film and convection cooling design are shown in Fig. 29-32. From the cooling distribution diagram, the hottest section can be seen to be the trailing edge. The web, which is the most highly stressed blade part, is also the coolest part of the blade.

Major Cycles The major application of most gas turbines is in an open cycle in which air is the working medium. The gas turbine can either be a single-shaft unit or a multiple-shaft unit. The single-shaft unit is one in which the compressor, the gas generator turbine, and the power turbine are on a single shaft. The single-shaft units are used in most electrical generating services where constant speed application is the norm. Multiple shaft units can be two or three shaft units. In a two-shaft unit, the high-pressure turbine (gas generator turbine) is driving the air compressor, and the low-pressure turbine, which is on a separate shaft and only aerodynamically coupled, produces the output power. A three-shaft unit is used in designs with very high compressor-pressure ratios. The high pressure requires two compressors: a low-pressure compressor and a high-pressure compressor. The high-pressure compressor is driven by the high-pressure turbine; the low-pressure compressor is driven by the intermediate-pressure turbine; and the low-pressure turbine drives the output shaft. Multiple shaft turbines are used often in mechanical drives where the driven equipment needs to be operated over a wide speed range.

The advantage of a multiple shaft unit over a wide output speed range is that the compressor and the compressor turbines can be maintained at relatively constant speed (75–100 percent of design), while the power turbine (low pressure turbine) can be operated over a very wide speed range without a great loss in thermal efficiency for the entire gas turbine. Variable area nozzles are sometimes used to control the low-pressure turbine; the high pressure turbine is controlled by change in the fuel flow, which affects the turbine firing temperature.

The Simple Cycle The simple cycle, or the Brayton cycle, is the most common type of cycle being used in the gas-turbine field today. The overall efficiency of a cycle can be improved by increasing the pressure ratio or the turbine inlet temperature (firing temperature). Today's simple-cycle turbines have pressure ratios as high as 17:1 and firing temperatures of about 2300° F (1260° C). In a simple cycle, there is an optimum pressure ratio for a turbine-firing temperature giving the highest efficiency. The efficiency of the various components such as the compressor, combustor, and turbine affects the overall thermal efficiency; however, even if these components were 100 percent efficient, the thermal cycle efficiency would only approach that of a Carnot cycle, which is the most efficient cycle between any two temperatures. Figure 29-33 shows the effect of pressure ratio and turbine inlet temperature on power and efficiency of simple cycle gas turbines.

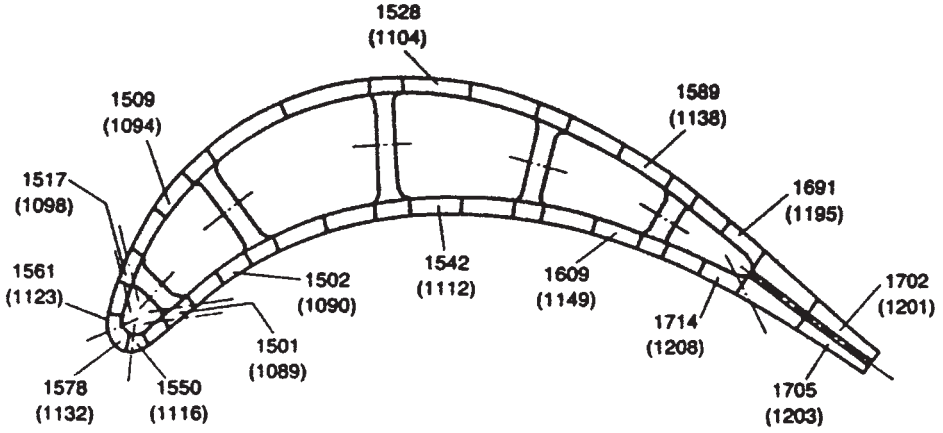


FIG. 29-32 Temperature distribution for film convection-cooled design, °F (cooled).

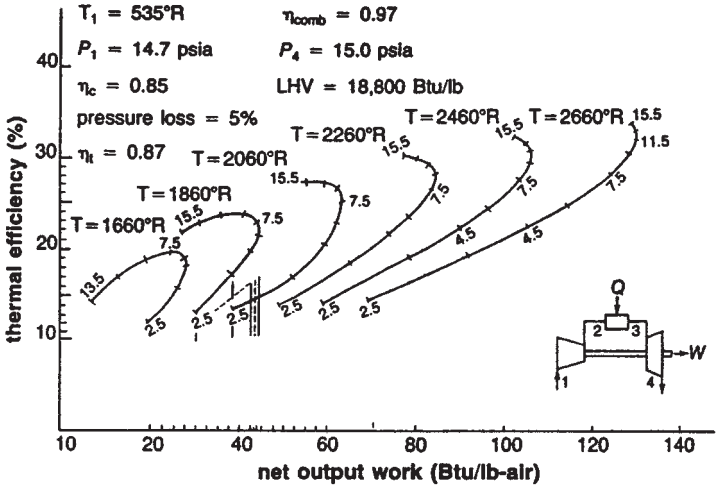


FIG. 29-33 Performance map showing the effect of pressure ratio and turbine inlet temperature on a simple cycle.

The Regenerative Cycle The regenerative cycle is becoming prominent in these days of tight fuel reserves and high fuel costs. The amount of fuel needed can be reduced by the use of a regenerator in which the hot turbine exhaust gas is used to preheat the air between the compressor and the combustion chamber. The regenerator increases the temperature of the air entering the burner, thus reducing the fuel-to-air ratio and increasing the thermal efficiency. For a regenerator assumed to have an effectiveness of 80 percent, the efficiency of the regenerative cycle is about 40 percent higher than its counterpart in the simple cycle, as seen in Fig. 29-34. The work output per pound of air is about the same or slightly less than that experienced with the simple cycle. The point of maximum efficiency in the regenerative cycle occurs at a lower pressure ratio than that of the simple cycle, but the optimum pressure ratio for the maximum work is the same in the two cycles.

The Reheat Cycle The regenerative cycle improves the efficiency of a gas turbine but does not provide any added work per pound of air flow. To achieve this latter goal, the concept of the reheat cycle must be utilized. The reheat cycle utilized in the 1990s has pressure ratios of as high as 30:1 with turbine inlet temperatures of about 2100° F (1150° C). The reheat is done between the power turbine and the compressor trains. The reheat cycle, as shown in Fig. 29-35, consists of a two-stage turbine with a combustion chamber before each stage. The assumption is made that the high-pressure turbine is only to drive the compressor and that the gas leaving this turbine is then reheated to the same temperature as in the first combustor before entering the low-pressure or power turbine.

The Intercooled Regenerative Reheat Cycle The Carnot cycle is the optimum cycle between two temperatures, and all cycles try to approach this optimum. Maximum thermal efficiency is achieved by approaching the isothermal compression and expansion of the Carnot cycle or by intercooling in compression and reheating in the expansion process. The intercooled regenerative reheat cycle approaches this optimum cycle in a practical fashion. This cycle achieves the maximum efficiency and work output of any of the cycles described to this point. With the insertion of an intercooler in the compressor, the pressure ratio for maximum efficiency moves to a much higher ratio, as indicated in Fig. 29-36.

The Steam Injection Cycle Steam injection has been used in reciprocating engines and gas turbines for a number of years. This cycle may be an answer to the present concern with pollution and higher efficiency. Corrosion problems are the major hurdle in such a system. The concept is simple and straightforward: Steam is injected into the compressor discharge air and increases the mass flow rate

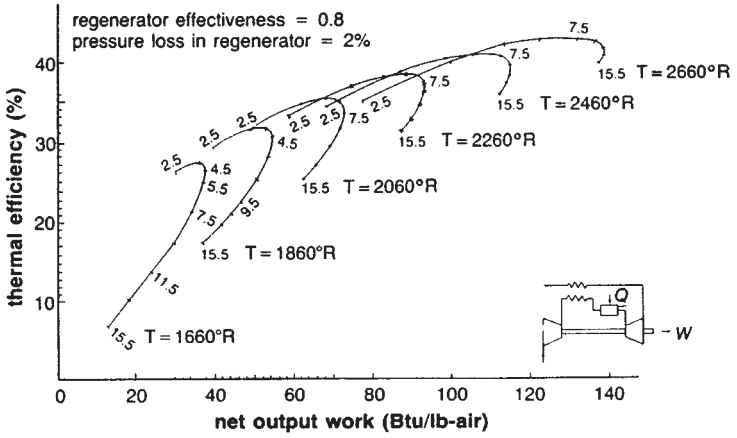


FIG. 29-34 Performance map showing the effect of pressure ratio and turbine inlet temperature on a regenerative cycle.

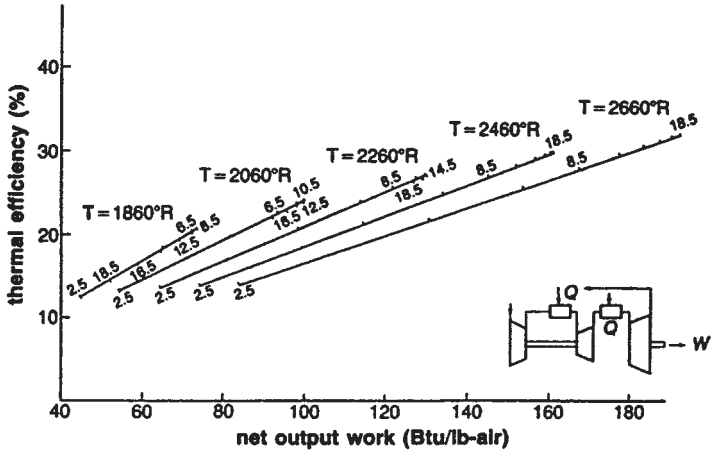


FIG. 29-35 Performance map showing the effect of pressure ratio and turbine inlet temperature on a split-shaft reheating cycle.

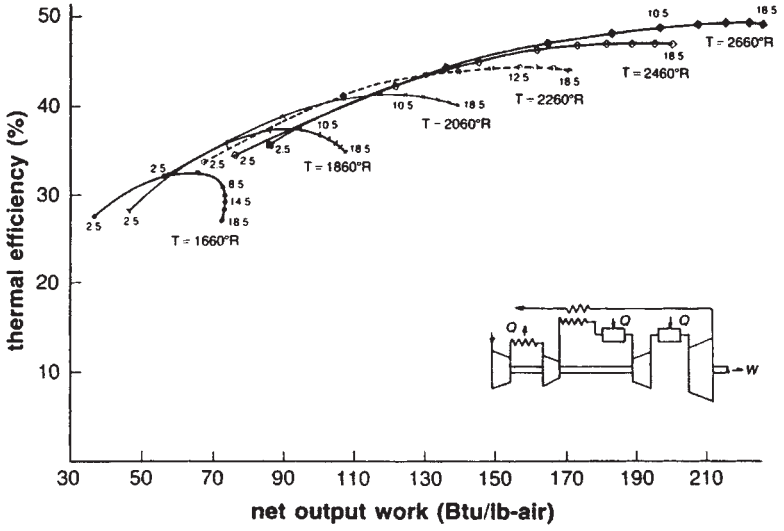


FIG. 29-36 Performance map showing the effect of pressure ratio and turbine inlet temperature on an intercooled regenerative reheat split-shaft cycle.

through the turbine. The steam being injected downstream from the compressor does not increase the work required to drive the compressor. The steam used in this process is generated by the turbine exhaust gas. Typically, water at 14.7 psi (101 kPa) and 80° F (27° C) enters the regenerator, where it is brought up to 60 psi (413 kPa) above the compressor discharge and the same temperature as the compressor discharge air. The steam is injected after the compression but far upstream of the burner to create a proper mixture.

For NO_x control only, steam is injected into the combustor directly to help reduce the primary zone temperature in the combustor. The amount of steam injected is in a ratio of 1:1 with the fuel. In this cycle, the steam is injected upstream of the combustor and can be as much as 5–8 percent by weight of the air flow. This cycle leads to an increase in output work and a slight increase in overall efficiency. Corrosion problems due to steam injection have been for the most part overcome with new high temperature coatings. Figure 29-37 shows the increase in efficiency and work output for various steam flow rates at a fixed turbine inlet temperature. Figure 29-38 shows the effect of 5 percent steam injection at various turbine firing temperatures.

The Combined (Brayton-Rankine) Cycle The 1990s has seen the rebirth of the combined cycle, the combination of gas turbine technologies with the steam turbine. This has been a major shift for the utility industry, which was heavily steam-turbine-oriented with the use of the gas turbine for peaking power. In this combined cycle, the hot gases from the turbine exhaust are used in a heat recovery steam generator or in some cases in a supplementary fired boiler to produce superheated steam.

The combined cycle work is equal to the sum of the net gas turbine work and the steam turbine work. About one-third to one-half of the design output is available as energy in the exhaust gases. The exhaust

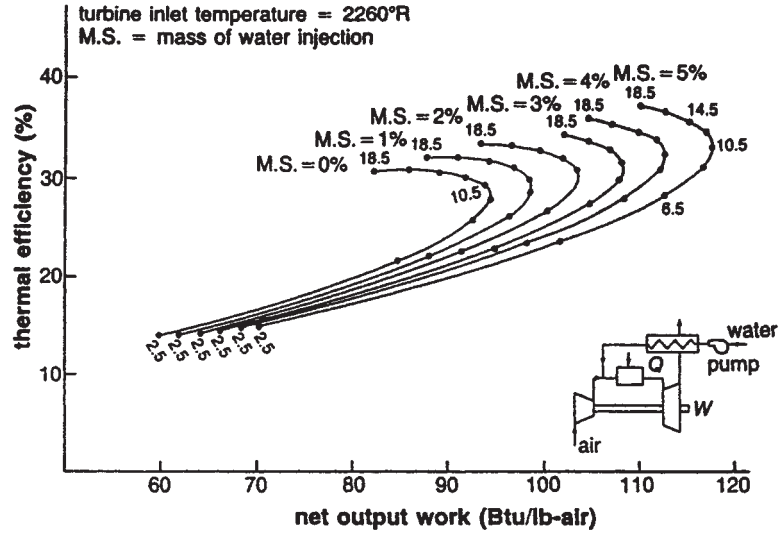


FIG. 29-37 Performance map showing the effect of pressure ratio and steam flow rate on a steam injection cycle.

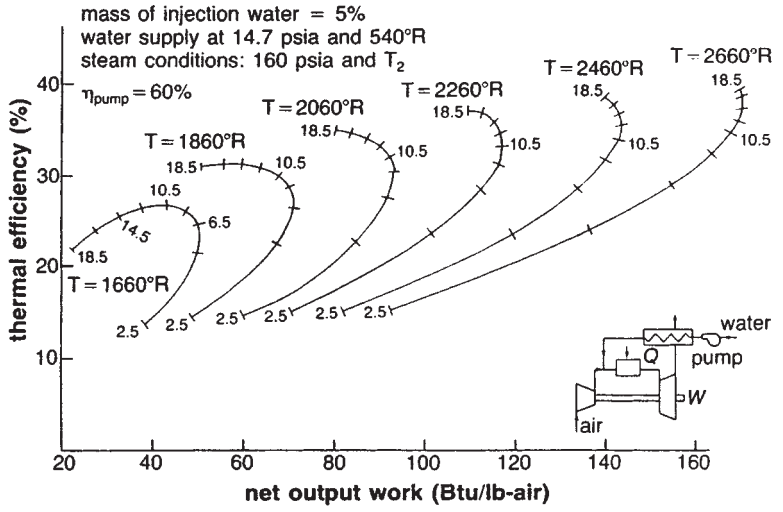


FIG. 29-38 Performance map showing the effect of pressure ratio and turbine inlet temperature on a fixed steam rate in a steam injection cycle.

gas from the gas turbine is used to provide heat to the recovery boiler. Thus, this heat must be credited to the overall cycle. This makes the combined cycle the highest practical efficiency cycle today. Figure 29-39 shows the effect of this cycle on the overall plant efficiency. To reduce the NO_x effect in the gas turbine, steam is injected in the combustor at a ratio of 1:1 with the fuel.

A comparison of the effect of the various cycles on the overall thermal efficiency is shown in Fig. 29-40. The most effective cycle is the Brayton-Rankine (combined) cycle. This cycle has tremendous potential in power plants and in the process industries where steam turbines are in use in many areas. The initial cost of the combined cycle is between \$800–\$1200 per kW while that of a simple cycle is about \$300–\$600 per kW. Repowering of existing steam plants by adding gas turbines can improve the overall plant efficiency of an existing steam turbine plant by as much as 3 to 4 percentage points.

Typically an inlet pressure decrease of one inch of water column reduces the power output by 0.4 percent and increases the heat rate by 0.125 percent. Similarly, an exhaust pressure increase of one inch of water reduces the power output by 0.15 percent and the heat rate by 0.125 percent.

TURBINE OPERATION CHARACTERISTICS

The gas turbine is a high-volume air machine. The compressor air power required is usually between 50–70 percent of the total power produced by the turbine. Thus, the ambient temperature affects the output of the gas turbine. On hot days, the gas turbine produces less output than on cold days. In dry climates, the use of evaporative cooling in the gas turbine decreases the effective inlet temperature and increases the power output of the unit.

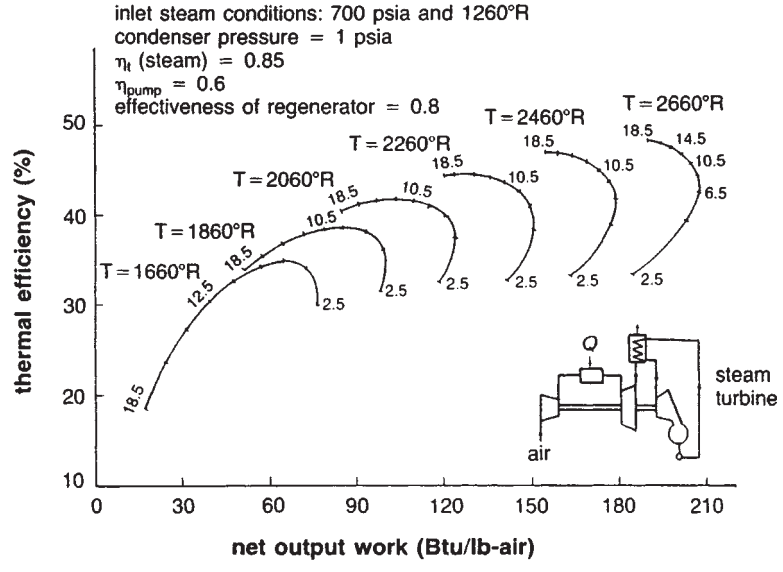


FIG. 29-39 Performance map showing the effect of pressure ratio and turbine inlet temperature on a Brayton-Rankine cycle.

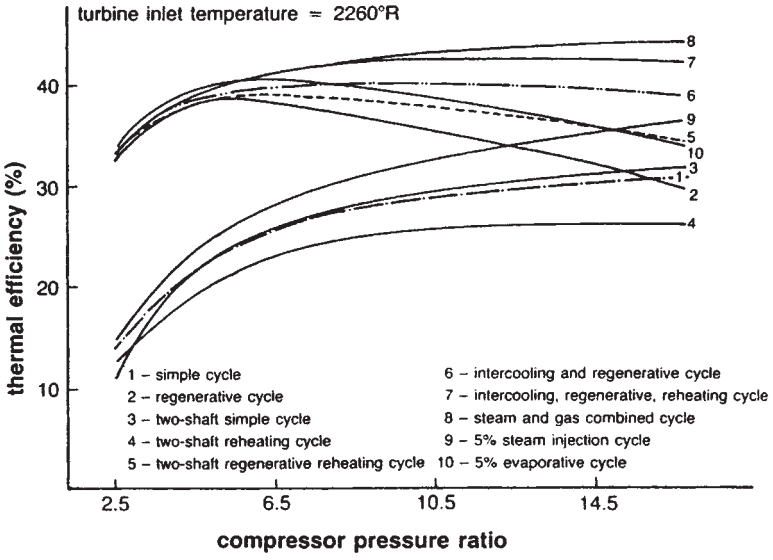


FIG. 29-40 Comparison of thermal efficiency of various cycles.

The effect on the performance of the inlet and exit conditions of the gas turbine is predominant. A increase in the inlet temperature by 5° F (2.8° C) will reduce the design power output by 2 %, and a reduction in the inlet pressure by 1 psi (6.9 kPa) would reduce the output by approximately 3 percent. Also, a 1 percent change in compressor efficiency reduces the overall thermal efficiency by ½ percent and reduces the power output by 2 percent. A 1 percent change in the turbine efficiency will produce a change of about 3 percent in turbine power output and a 0.75 percent change in the overall thermal efficiency. It is therefore very important to maintain the compressor in a very clean state. To do this, water solvent on-line cleaning is carried out on the compressor. Water jet nozzles are placed at the periphery of the compressor inlet. This type of cleaning is effective only on the first few stages. Coating the compressor blades has been found to improve efficiency. Inlet and outlet ducting should be designed with minimum losses; however, good filtration should not be compromised.

The gas turbine is usually started by an auxiliary drive such as a steam turbine, diesel engine, turboexpander, or electric motor. These drives bring the turbine up to a speed of between 1200–2000 rpm, at which time fuel is injected and the turbine speed is increased rapidly as the turbine firing temperature increases. The power requirement for the starter is about 5–10 percent of the power rating of the unit. Most turbine control systems have an acceleration monitor that shuts down the turbine if an acceleration rate is not maintained. *This is very essential if combustion in the turbine nozzles and blades is to be avoided.* To avoid compressor surges during startup and shutdown, a series of bleed valves in the compressor are sequentially closed at various speeds during the startup or are opened at various speeds during the shutdown. These bleed valves also are used for directing cooling air to the various regions of the turbine. Bleed valves are located in the early stages (i.e., 5th or 6th stage) and in the latter stages (i.e., 11th or 12th stage) of an axial flow compressor.

Multiple-shaft turbines require a little more starting power than single-shaft turbines. The low pressure turbine reaches breakaway torque at about 50–60 percent of the design speed of the gas generator section. In cases of aborted starts, the gas turbine must be fully purged before another start is attempted; otherwise, the gas trapped in the turbines could explode. In many new gas turbines, the first 5–7 stages of the compressor have variable stators that change angles at various settings. These move with speed and thus reduce the losses encountered in the compressor section.

In the case of the steam-injected cycle, steam must be injected after the turbine has been brought up to full speed; otherwise, compressor surges could occur. Major temperature excursions during startups must also be avoided to prevent degradation of the life of the turbine.

Life Cycle The gas turbine life and especially hot section life are significantly influenced by the following parameters:

1. Blade material and cooling flow (blade metal temperature)
2. Type of fuel
3. Number of starts and full load trips

BLADE MATERIALS

Turbine life is very sensitive to blade metal temperature and blade material. It is essential for prevention of hot corrosion to keep this temperature below 1400° F (760° C). This temperature is a function of cooling flow to the blades, and the firing temperature. The effect of cooling flow blockage can be catastrophic for these blades. The life of the blades, especially on rotating elements, is a function of blade stresses and metal temperature. The Larson Miller curve shown in Fig. 29-39 for typical turbine blade alloys shows the logarithmic relationship between these parameters. While widely used to describe an alloy's stress rupture characteristic over a side temperature life and stress range, it is also very useful in comparing the elevated temperature capabilities of many alloys. Turbine blade alloys, which usually have large quantities of Ni, Cr, and Co, tend to indicate low durability at operating temperatures. This results in surface notches initiated by erosion or corrosion, after which cracks are propagated rapidly. This often leads to high cycle and low stress failure.

Turbine blade coatings can extend the life of blades by nearly 70–80 percent. Coating prevents corrosion from attacking the base metal. Most present-day coatings are diffusion-packed-type coatings. They usually consist of a thin uniform layer of a precious metal (platinum) electroplated onto the blade surface. This procedure is followed by pack diffusion steps to deposit layers of aluminum and chromium, resulting in a coating that has an outer skin of an extremely corrosion-resistant, platinum-aluminum intermetallic composition. The gas turbines of the 1990s are all coated, especially in the hot section area. Coatings are also being applied to the compressor blades and have been found to be very effective.

TYPES OF FUEL

The life of a gas turbine depends heavily on the type of fuel used. An inherent fuel flexibility is the gas turbine's major advantage. Gaseous fuels traditionally include natural gas, process gas, and low-Btu gas

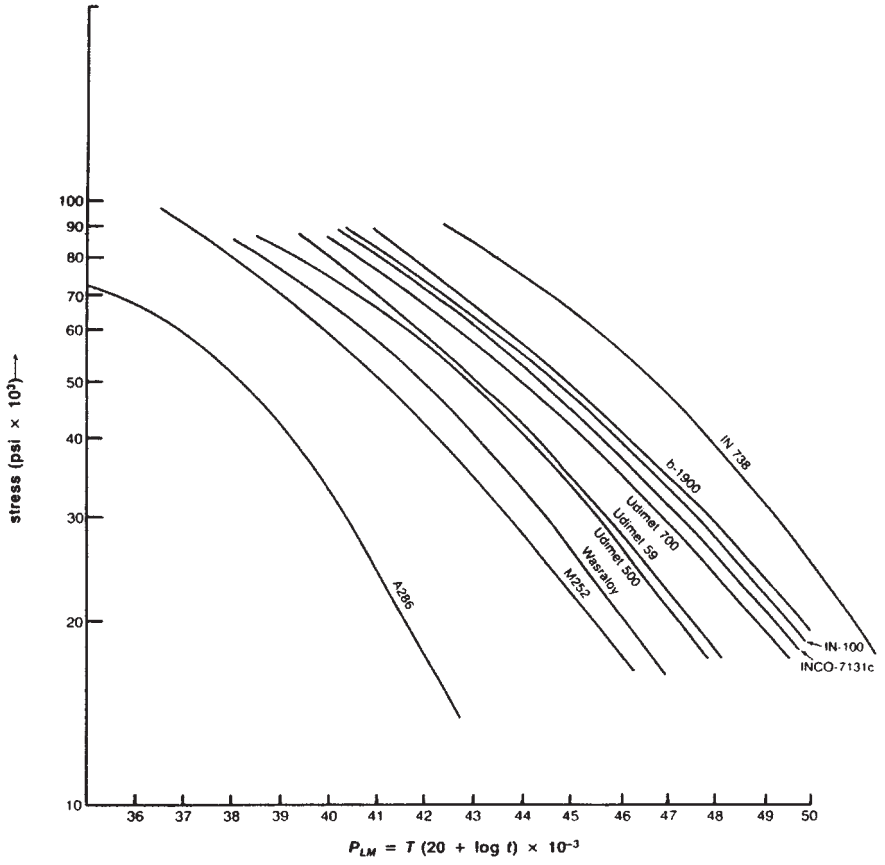


FIG. 29-41 Larson-Miller parameters for turbine blade alloys.

(coal gas or water gas). Natural gas is the benchmark against which performance of a gas turbine is compared, since it is a clean fuel that promotes long machine life.

Liquid fuels vary from light volatile fuels such as naphtha through kerosene to the heavy viscous residuals. True distillate fuel such as #2 distillate oil is a good fuel; however, because trace elements such as vanadium, sodium, potassium, lead, and calcium are found in the fuel, the fuel has to be treated. The corrosive effect of sodium and vanadium is very detrimental to the life of a turbine. Vanadium originates as a metallic compound in crude oil and is concentrated by the distillation process into heavy oil fractions. Sodium compounds are usually present in the form of salt water, which results from salty wells, transport over seawater, or mist ingestion in an ocean environment. Fuel treatments are costly and do not remove all traces of the metal. Sodium is usually removed by water washing and letting the sodium dissolve into the water. It is then separated by a centrifuge. Vanadium is counteracted by the addition of magnesium which causes a friable deposit. A magnesium/vanadium ratio of 3:1 reduces corrosion by a factor of six.

The typical amounts of sodium and vanadium in the fuel should be less than 1 ppm. Figure 29-42 shows the effect of sodium and vanadium on the life of the blade and on the combustor life. Figure 29-43 shows the reduction in firing temperature required to maintain design life (hrs) of a typical turbine (IN718) blade due to sodium and vanadium in the fuel.

In general terms, the life of a combustor might be reduced by about 30 percent through use of a distillate fuel and by 80 percent through the use of residual fuel. The first stage turbine nozzle life can be reduced by 20 percent through use of a distillate fuel and by about 65 percent when certain residual fuels are used.

Number of Starts and Full-Load Trips Temperature differentials developed during starting and stopping of the turbine produce thermal stresses. The cycling of these thermal stresses causes thermal fatigue. Thermal fatigue is a low cycle event and is similar to creep rupture failure. The analysis of thermal fatigue is essentially a problem in heat transfer and is affected by properties such as modulus of elasticity, coefficient of thermal expansion, and thermal conductivity. The most important metallurgical factors are ductility and toughness.

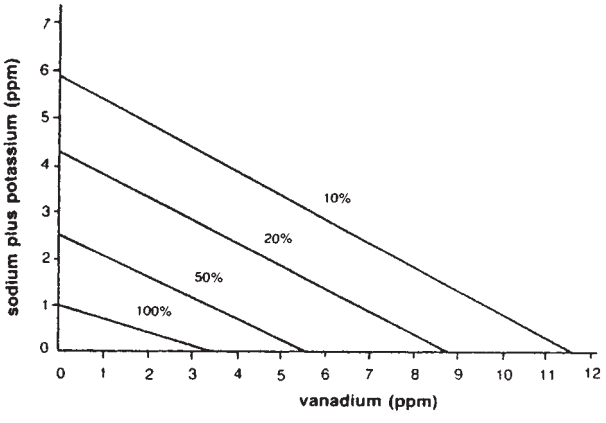


FIG. 29-42 Effect of sodium, potassium, and vanadium on combustor life.

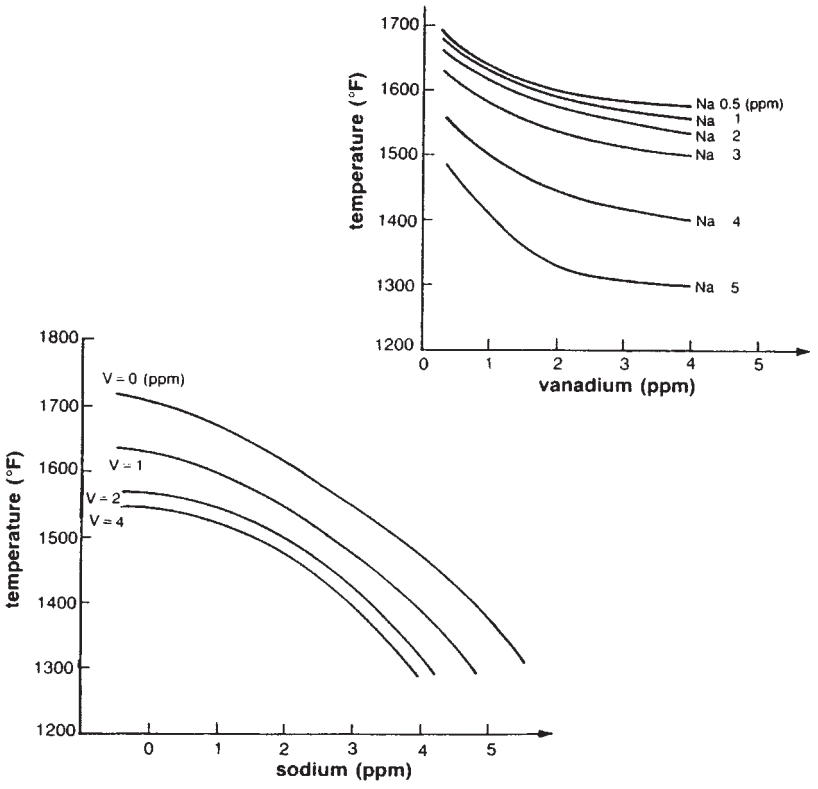


FIG. 29-43 Firing temperature reduction needed to offset IN 718 corrosion by sodium and vanadium.

Highly ductile materials tend to be more resistant to thermal fatigue and also seem more resistant to crack initiation and propagation.

The operating schedule of a gas turbine produces low-frequency thermal fatigue. The number of starts per hours of operating time directly affects the life of the hot sections (combustor, turbine nozzles, and blades). The life reduction effect of the number of starts on a combustor liner could be as high as 230 hours/start and on the turbine nozzles as high as 180 hours/start. The effect of full load trips can be nearly 2–3 times as great!

The life of a gas turbine depends on the above detailed operational characteristic. It is interesting to note that, for a gas turbine life of 25 years, the life cycle costs can be distributed as 5–10 percent on initial cost, 10–20 percent on maintenance costs and 70–85 percent on cost of fuel. Gas turbines will be very widely used in the 21st century in combined cycle applications as the power source for the world. These combined cycle plants will have efficiencies in the high fifties and will cost between $1000 and $1200 per kW, using 1994 as a monetary benchmark.

EXPANSION TURBINES

Fundamentally, an expansion turbine is a device for converting the pressure energy of a gas or vapor stream into mechanical work as the gas or vapor expands through the turbine. The mechanical work so produced, however, is generally a by-product, the primary objective of the turboexpander being to chill the process gas. Turboexpanders are in wide use in the cryogenic field to produce the refrigeration required for the separation and liquefaction of gases.

By common usage, the terms "turboexpanders" and "expansion turbines" specifically exclude steam turbines and combustion gas turbines, which are covered elsewhere in Sec. 29.

Any work developed by the turboexpander is at the expense of the enthalpy of the process stream, and the latter is correspondingly cooled. A low inlet temperature means a correspondingly lower outlet temperature, and the lower the temperature range, the more effective the expansion process becomes.

FUNCTIONAL DESCRIPTION

The turboexpander in combination with a compressor and a heat exchanger functions as a heat pump and is analyzed as follows: In Fig. 29-44 consider the compressor and aftercooler as an isothermal compressor operating at T_2 with an efficiency E_c, and assume the working fluid to be a perfect gas. Further, consider the removal of a quantity of heat Q_e by the turboexpander at an average low temperature T_1. This requires that it deliver shaft work equal to Q_e. Now, make the reasonable assumption that one-tenth of the temperature drop in the expander is used for the temperature difference in the heat exchanger. If the expander efficiency is N_e and this efficiency is multiplied by 0.9 to include the effect of the temperature difference in the heat exchanger, the needed ideal enthalpy drop across the expander is

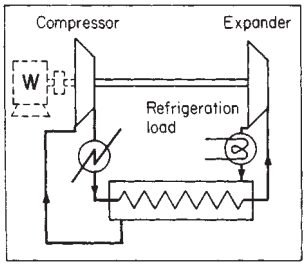


FIG. 29-44 Turboexpander system functioning as a refrigeration machine.

$$H_e = Q_e/0.9N_e \tag{29-16}$$

The theoretical required (isothermal) compression work in the compressor, which is assumed to operate isothermally at T_2, is

$$(Q_e/0.9N_e)(T_2/T_1) \tag{29-17}$$

The actual compressor work W_c is this latter quantity, divided by the compressor isothermal efficiency N_c; thus,

$$W_c = (Q_e/0.9N_eN_c)(T_2/T_1) \tag{29-18}$$

Mechanical work equal to $Q_e/0.9$ is returned by the expander to the compressor, so the net work to the compressor is

$$W = W_c - \frac{Q_e}{0.9} = \left(\frac{Q_e}{0.9}\,\frac{T_2}{N_eN_cT_1}\right) - \frac{Q_e}{0.9}$$

$$W = \left(\frac{Q_e}{0.9}\,\frac{T_2}{N_eN_cT_1}\right) - 1 = \frac{Q_e}{0.9}\left(\frac{T_2 - N_eN_cT_1}{N_eN_cT_1}\right) \tag{29-19}$$

The second-law theoretical work is

$$W_{\text{theor}} = Q_e\,\frac{T_2 - T_1}{T_1} \tag{29-20}$$

Hence, the second-law efficiency of the expander-heat-exchanger-compressor system is

$$\frac{W_{\text{theor}}}{W} = \frac{Q_e\,\dfrac{T_2 - T_1}{T_1}}{\dfrac{Q_e}{0.9}\left(\dfrac{T_2 - N_eN_cT_1}{N_eN_cT_1}\right)}$$

$$= \frac{0.9(T_2 - T_1)N_eN_c}{T_2 - N_eN_cT_1} \tag{29-21}$$

A plot of this efficiency in which commonly available equipment is assumed is shown by the expander curve in Fig. 29-45.

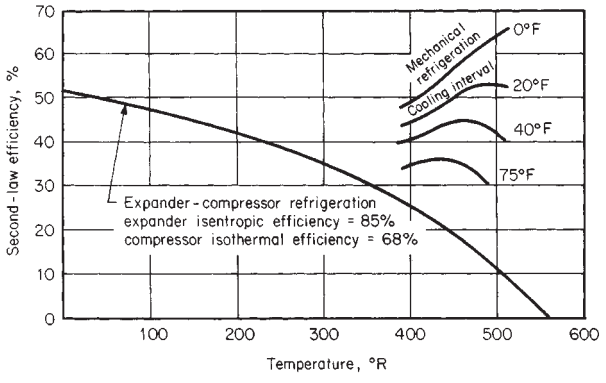


FIG. 29-45 Mechanical versus turboexpander refrigeration. K = 5/9°R; °C = 5/9(°F − 32).

The family of short curves in Fig. 29-45 shows the power efficiency of conventional refrigeration systems. The curves for the latter are taken from the *Engineering Data Book*, Gas Processors Suppliers Association, Tulsa, Oklahoma. The data refer to the evaporator temperature as the point at which refrigeration is removed. If the refrigeration is used to cool a stream over a temperature interval, the efficiency is obviously somewhat less. The short curves in Fig. 29-45 are for several refrigeration-temperature intervals. A comparison of these curves with the expander curve shows that the refrigeration power requirement by expansion compares favorably with mechanical refrigeration below 360° R (–100° F). The expander efficiency is favored by lower temperature at which heat is to be removed.

Another conclusion that can be drawn from Fig. 29-45 is that if the process can justify the complexity, it is more efficient, powerwise, to use conventional means rather than expanders to absorb heat at moderate temperatures in the range of ambient to 360° R, although for expediency expanders are frequently used in any case.

SPECIAL CHARACTERISTICS

An example of a typical turboexpander is shown in Fig. 29-46. Radial-flow turbines are normally single-stage and have combination impulse-reaction blades, and the rotor resembles a centrifugal-pump impeller. The gas is jetted tangentially into the outer periphery of the rotor and flows radially inward to the "eye," from which the gas is jetted backward by the angle of the rotor blades so that it leaves the rotor without spin and flows axially away.

Radial-flow turbines have been developed primarily for the production of low temperatures, but they also may be used as power-recovery devices.

The characteristics of these machines include the following:

1. High efficiency: 75 to 88 percent
2. Operation usually at a very low temperature
3. Operation often on small or moderate streams, dictating a rather high rotating speed
4. Supports having low heat conductivity
5. Effective shaft seals to conserve the process stream
6. Heavy-duty construction resistant to abuse
7. High reliability

Commonly established operating limitations for turboexpanders without special design features are an enthalpy drop of 93 to 116.3 kJ/kg (40 to 50 Btu/lb) per stage of expansion and a rotor-tip speed of 304.8 m/s (1000 ft/s). Commercial turboexpanders are available for inlet pressure up to 20.68 MPa (3000 lbf/in^2) and inlet temperatures from near absolute zero to 538° C (1000° F). The permissible liquid condensation in the expanding stream varies with discharge pressure; it may be 50 weight percent or higher in the discharge, provided the turboexpander has been specially designed to handle condensation.

RADIAL INFLOW DESIGN

The radial reaction design has been selected for turboexpanders primarily because it attains the highest efficiency of all turbine designs. However, it has several additional features which favor this application:

1. In the single-stage configuration, it is usual to have the rotor on the end of the shaft (overhung); this provides a convenient opportunity for thermally insulating the cold turbine portion and is an ideal arrangement for axial discharge.
2. This design permits variable primary nozzles, which enable the attainment of high efficiency over a wide flow range.
3. It applies lower axial thrust to the shaft than a single-stage axial reaction turbine.
4. It has shaft bearings on only one side of the expander rotor, and heat-barrier insulation between the warm, lubricated bearings and the cold turbine is convenient to arrange.
5. Its speed is reasonably acceptable for suitable loading devices.

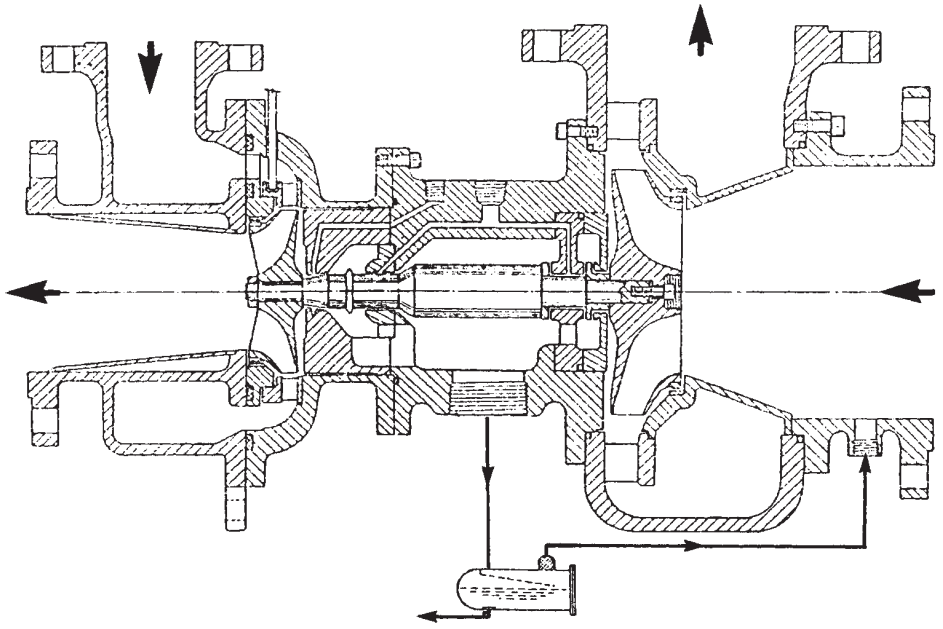


FIG. 29-46 Typical radial-flow turboexpander.

EFFICIENCY

Efficiency for a turboexpander is calculated on the basis of isentropic rather than polytropic expansion even though its efficiency is not 100 percent. This is done because the losses are largely introduced at the discharge of the machine in the form of seal leakages and disk friction which heats the gas leaking past the seals and in exducer losses. (The exducer acts to convert the axial-velocity energy from the rotor to pressure energy.)

BEARINGS

Radial Bearings Antifriction bearings are largely unsuitable for these applications, chiefly because of the special attention and maintenance which they demand.

Virtually all expanders have lubricated sleeve bearings or tilting-shoe bearings. The advantage of sleeve bearings is that they can be designed to support the shaft sufficiently rigidly that the oil-film critical (first critical) can be designed to be safely above the design running speed. This is desirable because it eliminates all shaft vibrations in the full operating range; more important, if the critical were below the design speed, then at design speed the shaft assembly would be rotating about its center of gravity. In turboexpanders, there frequently are ice deposits or other reasons for rotor imbalance, and such imbalance would cause gyration and damage to the shaft seals.

In arrangements in which the shaft is running with its first critical (oil-film critical) below the design speed, then not far above design speed is the oil swirl (half-speed gyration). Substitution of tilting-shoe bearings for sleeve bearings moves the oil swirl to a higher speed, but it does not prevent the rotor from rotating about its center of gravity. Tilting-shoe bearings do not lubricate well at this high rubbing speed and small shaft diameter.

The sleeve bearing has the further advantage that it functions as a lubricated, pressurized shaft seal to contain the pressure on the process gas (see subsection "Shaft Seals").

Thrust Bearings Turboexpanders often have process upsets or ice plugging or the like, which can cause serious thrust-bearing load variations. In applications above 506.6 to 1013.2 kPa (75 –148 psi), the best available thrust bearing usually is insufficient to protect against such high thrust loads. Various indications, such as the differential pressure across the rotor and thrust-bearing temperatures, are available to protect the unit at least to some extent.

Thrust-bearing-load meters for protection against excessive loading are available on thrust bearings, and automatic thrust control, which functions by controlling the pressure behind a balancing drum, also is available.

SEALS

Shaft Seals Mechanical shaft seals generally are not acceptable in turboexpanders for the same general reason that antifriction bearings are not: they require periodic replacement and careful attention. In their stead, close-clearance labyrinth-type seals are generally used. Such a labyrinth seal generally has an injection point intermediate from its two ends into which a suitable buffer gas is injected to prevent the escape of the process gas; instead, buffer gas escapes. If the escaping seal gas is inexpensive and nontoxic, it may be allowed to leak to the atmosphere. However, it is possible to enclose the expander housing to the bearing housing and allow the journal bearing, acting as an oil seal, to contain the outleaking seal gas and collect it in a float-operated drainer for suitable disposal or reuse.

In refrigeration applications in which the refrigerant must be completely conserved, the expander housing and bearing housing can be hermetically sealed through a speed-reducing gearbox. The low-speed shaft of the gearbox is sealed with a low-speed mechanical seal. Then any refrigerant which leaks out of the labyrinth seal is totally contained in the gearbox and in the closed lubrication system for complete collection and reuse.

Rotor Seals To balance the thrust on the rotor, usually there are one or two labyrinth-type seals on the rotor. These seals often are damaged if there is dust in the incoming fluid or gas, and wear on the backside seal causes serious upsets in thrust-bearing loads. Provisions are available for collecting and disposing of the dust which tends to accumulate in the seal so as to protect the seal from serious erosion.

VARIABLE NOZZLES

The pressurized process stream is guided radially into the rotor by the primary nozzles, which are a series of vanes forming nozzles jetting the gas tangentially and inwardly into the rotor (see Fig. 29-47). These

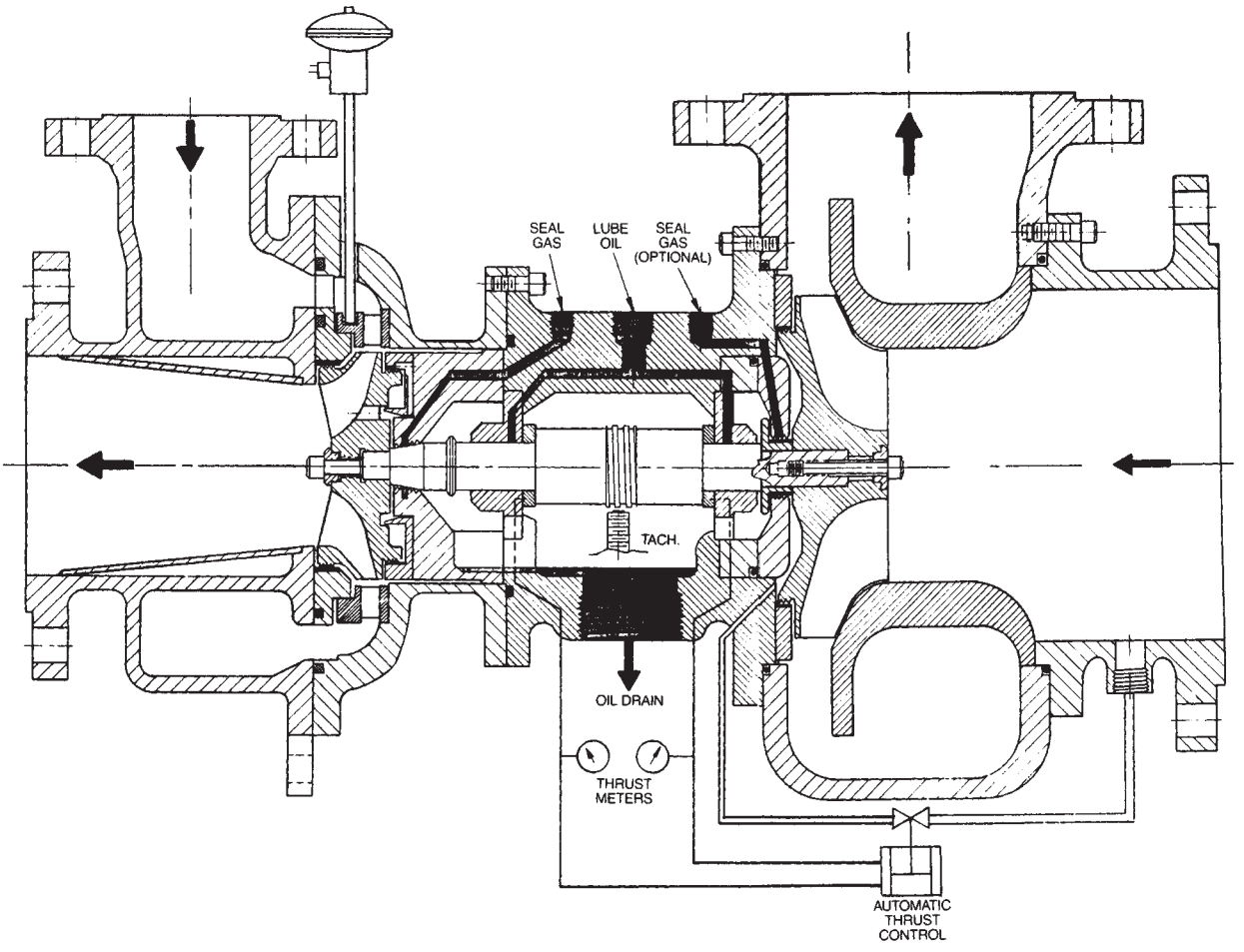


FIG. 29-46 (*Continued*) Typical radial-flow turboexpander.

nozzle vanes are clamped between two flat rings and usually are pivoted so that they can be rotated in unison to open or close the spaces between them in order to vary the nozzle-throat areas. This is quite an important function because it can be used to vary the flow widely through the expander without wasteful throttling: all the expansion energy in the nozzles is recovered in the rotor. The variable nozzles, from a control standpoint, act just as a throttle valve would act in controlling the flow (but without throttling loss), and conventional flow-control instrumentation can be used to operate them.

ROTOR RESONANCE

Variable nozzles produce a series of jets of gas entering the rotor, and these impulses add up to form a frequency equal to the blade-passing frequency: the number of revolutions per second multiplied by the number of nozzle vanes, which is of the order of thousands of cycles per second. Frequently the rotor will resonate at this frequency, and if it does, it will be fatigued and crack and break up; thus these frequencies must be avoided, and the manufacturer should be asked to supply information to the customer on this subject.

CONDENSING STREAMS

It is advantageous to have the expander generate its refrigeration at the lowest possible temperature in the process (see Fig. 29-45), and this frequently encounters the condensation temperature of the process stream. Steam-turbine practice advises against operating on condensing streams because efficiency is deteriorated and there also usually is erosion of the rotor blades.

Another advantage of the radial reaction turbine is that it can be designed to accept condensation in any amount without efficiency deterioration or erosion.* This is possible because there are two forces acting on suspended fog particles, the deceleration force and the centrifugal force, and these two forces can be balanced against each other to prevent the droplets from impinging on specially shaped blades. The process is explained as follows:

This expansion of a condensing vapor is highly desirable thermodynamically, but the liquid must not bombard and erode the rotor blades, and, in particular, it must not accumulate in the rotor, since that would cause efficiency loss.

If liquid droplets form as the gas is expanded in the turboexpander, one's first thought may be that a radial inflow design is the last thing to use, but the following explanation will show that this is the only design that can accomplish expansion efficiently.

Figure 29-47 shows the primary nozzles and the rotor. About half of the pressure drop takes place in the primary nozzles, which jet the gas tangentially into the periphery of the rotor. Cooling takes place during this expansion, and the jetted stream entering the rotor may be foggy. This foggy gas flows radially inward within the rotor as the latter rotates, and at the outlet, which is near the center of the rotor, the

* This same principle applies also to the expansion of flashing liquids in which the bubbles are guided away from the blades.



FIG. 29-47 The primary nozzles and the rotor.

fluid is discharged by being jetted backward out of the rotor so as to leave without rotary motion. The second half of the expansion energy is spent by the gas passing radially through the rotor against centrifugal force, and further precipitation of liquid takes place.

The stream from the nozzles enters the rotor with a tangential velocity of about 152.4 or 304.8 m/s (500 or 1000 ft/s; see Fig. 29-48) and follows a path through the rotor of such curvature that the centrifugal force acting on an element of the stream and, therefore, on suspended droplets is of the order of 75,000 G (75,000 times the force of gravity). Also, the stream, because it is moving radially inward in the rotor, is decelerated in the rotor from this tangential velocity of 304.8 m/s (1000 ft/s) down to zero tangential velocity in about a half a revolution of the rotor. This deceleration force amounts to something like 10,000 G. The vector sum of these two forces, therefore, amounts to 75,000 or 100,000 G in a direction 5 to 15° from the radial direction (see Fig. 29-48). This is an acceptable direction for the blades to lie, so the problem of avoiding bombardment of the blades by the droplets is solved by shaping the expander rotor blades parallel to this resultant vector. Then there is no force causing droplets to drift in the direction of any surface. They do drift back upstream slightly but nevertheless are carried on through by the mainstream and discharged. By this method any amount of condensing liquid can pass through, or, in the case of flashing liquids being expanded, the bubbles can pass through without efficiency loss. It would be impossible to construct a turbine blade meeting this requirement without two vector forces.

APPLICATIONS

The important uses of turboexpanders are in:

1. Air separation
2. Recovery of condensables from natural gas
3. Liquefaction of gases, including helium

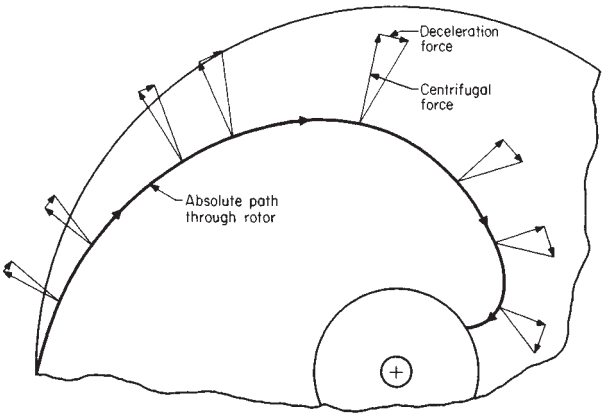


FIG. 29-48 Elemental path radially inward, then axially, through the rotor.

4. Augmenting refrigeration in various cryogenic processes such as the recovery of ethylene
5. Power generation, sometimes referred to as power recovery

A potential application for the turboexpander for power recovery exists whenever a large flow of gas is reduced from a high pressure to some lower pressure or when high-temperature process streams (waste heat) are available to boil a secondary liquid. When such conditions exist, they should be examined to see if use of a turboexpander is justified. In such cases a turboexpander can be used to drive a pump, compressor, or electric generator, thus recovering a large portion of otherwise wasted energy. In applications of this type, careful consideration should be given to the temperature drop which will occur in the expander. It may sometimes be necessary to heat or to dry the inlet gas to avoid low exhaust temperatures that cause the formation of ice or liquids.

Expanders are used because they are in an advanced state of development and reliability, attain high efficiency, and are relatively inexpensive.

LUBRICATION

Expander bearings are usually high-speed, and they should have full film lubrication. This is best assured by using force-feed lubrication at a pressure of the order of 689.5 kPa (100 lbf/in^2) or more. There is no special objection to using pressures as high as 6.895 MPa (1000 lbf/in^2) or higher, if for some reason it is desirable to do so.

Usually, a journal bearing and a thrust bearing are combined in one assembly, and oil is injected so as to feed both of them. The rate of flow usually is adjusted so as to carry the heat away with a temperature rise of the order of 11 to 17° C (20 to 30° F).

The smallest expanders usually use oil with a viscosity at 38° C (100° F) of 60 to 100 SSU, and large machines up to 500 SSU. If the oil is kept in a totally enclosed system in contact with hydrocarbon or another partly soluble gas, which would dissolve and reduce the viscosity of the oil, then a compensating higher viscosity should be used so that the working viscosity after ultimate equilibrium with such gas is suitable for the bearings.

The lubrication system, for reliability reasons, usually has an operating and a standby pump and dual switchable filters. If there is a cooling-water scaling problem, coolers may also be switchable.

BUFFER-GAS SYSTEM

The shaft seal (see subsection "Shaft Seals") generally is a close-clearance labyrinth-type seal. It is desirable that there be available a suitable pressurized buffer gas for injection into the intermediate point in the seal, such gas to be available at an absolute pressure well above the highest shaft pressure to be sealed. Then the seal-gas system may consist of only a filter, a flow-indicating device, and a throttle

valve or other flow or pressure control, usually a pressure regulator and a graduated needle valve.

If the available pressure is not far above that of the pressure to be sealed, then with simple throttling the flow may be insufficient when the two pressures come too near together. Then more precise control, such as by differential pressure between the process side and the seal-gas pressure, may be required.

SIZE SELECTION

Size, rotating speed, and efficiency correlate well with the available isentropic head, the volumetric flow at discharge, and the expansion ratio across the turboexpander. The head and the volumetric flow and rotating speed are correlated by the specific speed. Figure 29-49 shows the efficiency at various specific speeds for various sizes of rotor. This figure presumes the expansion ratio to be less than 4:1. Above 4:1, certain supersonic losses come into the picture and there is an additional correction on efficiency, as shown in Fig. 29-50.

The available isentropic head is usually calculated by computer, using any of the various equations of state. In the absence of such facility, a quick and reasonably reliable calculation follows. In fact, this calculation is valuable as a cross-check on other methods because it is likely to be accurate within a few percent.

R = gas constant, 1.986 T_a = average temperature, °R

Z_a = compressibility at T_a H_i = isenthalpic work,

$$H_i = \frac{RT_aZ_a}{\text{mol. wt.}} \ln \frac{P_1}{P_2} \quad \text{Btu/lb} \qquad (29\text{-}22)$$

where H_i = reversible incremental enthalpy drop, Btu/lb
R = gas constant, 1.986, Btu/(lb·mol·°R)
T_a = average temperature for the increment, °R
Z_a = average compressibility for the increment
P_1/P_2 = pressure ratio

The use of this equation requires that an average P and T, based on an assumed increment, be used to find Z.

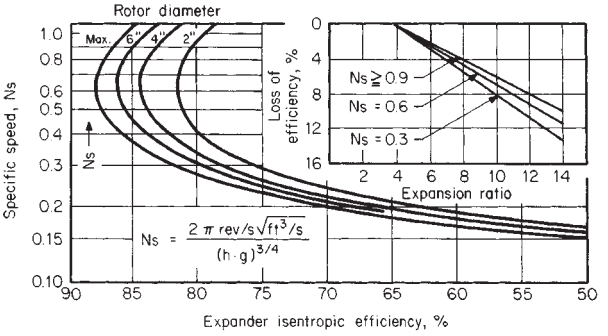


FIG. 29-49 Efficiency at various specific speeds for various sizes of rotor.

FIG. 29-50 Loss of efficiency as a function of the pressure ratio.

INSTRUMENTATION

Process-flow control and buffer-gas control have been discussed under "Variable Nozzles" and "Buffer-Gas System" respectively. Speed is usually self-controlled by a matching speed-sensitive load such as a compressor or a pump. If the load is an induction or synchronous generator feeding into a stable ac system, the system frequency fixes the speed. Otherwise, the speed can be controlled by a conventional governor.

Various protective instruments are used to provide a shutdown signal (to a fast-acting trip valve at the expander inlet) that senses various things, such as overspeed, lubricant pressure, bearing temperature, lubricant temperature, shaft runout, icing, lubricant level, thrust-bearing load, and process variables such as sensitive temperatures, levels, pressures, etc. However, too many safety shutdown devices may lead to excessive nuisance shutdowns.

POWER RECOVERY FROM LIQUID STREAMS

BASIC PRINCIPLES

The potential for power recovery from liquid streams exists whenever a liquid flows from a high-pressure source to one of lower pressure in such a manner that throttling to dissipate pressure occurs. Such throttling represents a system potential for power that is the reverse of a pump—in other words, a potential for power extraction. Just as in a pump, there exists a hydraulic horsepower and a brake horsepower, except that in the recovery they are generated or available horsepowers.

Basically, power recovery from liquids is achieved in industrial installation as shaft horsepower. While this potentially could appear either as reciprocating or as rotating power, most larger applications are rotating. Consideration of power recovery from liquids involves a choice among several possible uses, and usually this choice involves as alternatives (1) driving of a few large-horsepower services versus driving of more smaller-horsepower services; (2) driving of essential versus nonessential services or of spared versus nonspared services; (3) driving as sole driver versus partial driver or full horsepower versus partial horsepower for the selected service; and (4) converting power-recovery energy to some other intermediate energy form, as by driving an electric generator.

In applying power recovery, three basic problems are (1) limitations in designing equipment to recover the power, (2) operating reluctance to consider rotating equipment that is not absolutely necessary, and (3) the way in which the economics of the installed system is evaluated. It is important to recognize that there has always been an operable, acceptable alternative to power recovery from liquid streams in the form of the throttling or letdown valve, whereas no such simple, cheap, foolproof substitute exists for the pump.

Basic to establishing whether power recovery is even feasible, let alone economical, are considerations of the flowing-fluid capacity available, the differential pressure available for the power recovery, and corrosive or erosive properties of the fluid stream. A further important consideration in feasibility and economics is the probable physical location, with respect to each other, of fluid source, power-production point, and final fluid destination. In general, the tendency has been to locate the power-recovery driver and its driven unit where dictated by the driven-unit requirement and pipe the power-recovery fluid to and away from the driver. While early installations were in noncorrosive, nonerosive services such as rich-hydrocarbon absorption oil, the trend has been to put units into mildly severe services such as amine plants, hot-carbonate units, and hydrocracker letdown.

Economics Power-recovery units have no operating costs; in essence, the energy is available free. Furthermore, there is no incremental capital cost for energy supply. Incremental installed energy-system costs for a steam-turbine driver and supply system amount to about $800 per kilowatt, and the incremental cost of an electric-motor driver plus supply system is about $80 per kilowatt. By contrast, even the highest-inlet-pressure, largest-flow power-recovery machines will seldom have an equipment cost of more than $140 per kilowatt, and costs frequently are as low as $64 per kilowatt. However, at bare driver costs (not including power supply) of $64 to $140 per kilowatt for the power-recovery driver versus about $30 to $80 per kilowatt for

steam turbines or $50 to $64 per kilowatt for electric motors, operating costs must be considered to make power-recovery units attractive. Using commonly accepted values for power costs, turbine steam rates, and steam selling prices, operating costs for either motors or steam turbines approximate $280 per year for 746 W (1 hp).

Thus, barring technical difficulties or operational considerations in application, power-recovery units ought to show payouts of less than 6 months. Actual project payouts run from 1 to 3 years. This difference is due principally to (1) the fact that while the incremental costs just presented are valid in comparing large systems, specific designs encounter frame-size breaks, standardized capacities and horsepowers, code requirements, etc.; and (2) operating requirements, sparing considerations, and a certain lack of confidence in power-recovery units stemming from lack of extensive experience produce equipment-selection schemes that deviate from the straightforward comparison.

Development The following discussion relates specifically to the use of what could be called radial-inflow, centrifugal-pump power-recovery turbines. It does not apply to the type of unit nurtured by the hydroelectric industry for the large-horsepower, large-flow, low- to medium-pressure differential area of hydraulic water turbines of the Pelton or Francis runner type. There seems to have been little direct transfer of design concepts between these two fields; the major manufacturers in the hydroelectric field have thus far made no effort to sell to the process industries, and the physical arrangement of their units, developed from the requirements of the hydroelectric field, is not suitable to most process-plant applications.

Despite a rather slow start, centrifugal power-recovery pump-turbines have built a respectable record of process-plant installations extending back to the middle 1950s. Applications have included drives for the following services: cooling-tower fans; reciprocating recycle compressors; gas-treating-solution circulation pumps, as sole drive and as tandem with a steam turbine or motor helper; refinery-unit charge-stock pumps with a helper driver; and floating-online electric generators.

In general, early experiences were in the small-horsepower, nonessential or spared services, using sole drivers at full horsepower. The present trend is more and more toward the few large drivers in essential services, usually supplying only partial horsepower but not spared. If a plant is based on electric drivers and the economics of rate structure, demand charges, etc., permits, the use of a power-recovery unit driving a generator electrically floating on the line has found increasing favor. In general, operating experience in regard to reliability, serviceability, and maintainability has shown the units to be comparable with centrifugal pumps and has resulted in increasing acceptance even as drivers in large-horsepower units on essential service equipment. Presently accepted industrial limits are shown in Fig. 29-51.

Hydraulic Behavior The basic hydraulic behavior of centrifugal pumps operating as power-recovery units (turbines) is not much different from that of centrifugal pumps and follows the same sort of affinity laws over narrow ranges. Typical generalized curves are shown in Figs. 29-52 and 29-53. Note particularly that both torque and horsepower go negative (turn to values indicating power consumption) when head and capacity are within a fairly wide range representing at least startup and shutdown conditions if not also part load. Note also that even if head goes to 125 percent of design, speed (r/min) at zero torque for this unit does not exceed about 130 to 150 percent of design.

Tests conducted to operate centrifugal pumps as hydraulic turbines throughout the head-capacity-speed range show that a good centrifugal pump generally makes an efficient hydraulic turbine. From theoretical considerations it is possible to state that at the same speed

$$H_t = H_p/e_h^2 \tag{29-23}$$

$$Q_t = Q_p/e_h \tag{29-24}$$

$$n_{st} = n_{sp}e_h \tag{29-25}$$

where H = total head at best efficiency point
Q = capacity
n_s = specific speed

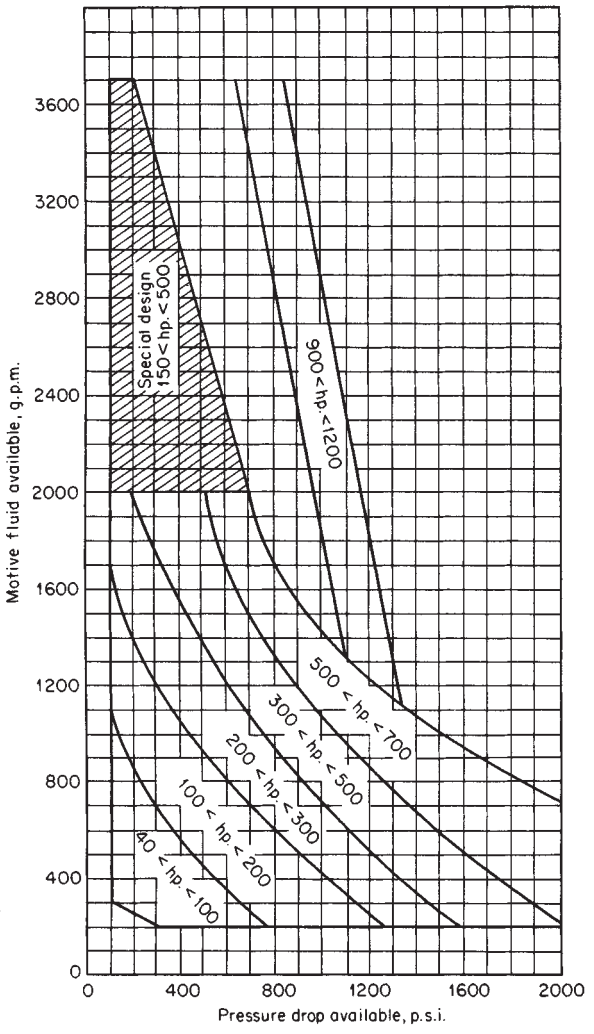


FIG. 29-51 Application areas for centrifugal pump turbines. Curves apply between the following minimum and maximum limits: inlet pressure, 100 to 3000 psig; pressure differential, 100 to 2800 lbf/in^2; flow of motive fluid, 200 to 4000 gal/min; horsepower, 50 to 3000 hp. Curve horsepower is based on a speed of 3600 r/min and a fluid of 1.0 specific gravity; for other fluids, multiply the curve horsepower by specific gravity to get the actual horsepower. To convert pounds-force per square inch to megapascals, multiply by 6.89×10^{-3}; to convert gallons per minute to cubic meters per minute, multiply by 3.79×10^{-3}; and to convert horsepower to kilowatts, multiply by 0.746.

e_h = hydraulic efficiency, taken as the same for the turbine and the pump
t, p = subscripts denoting turbine and pump respectively

Since the exact value of the **hydraulic efficiency** e_h is never known, $\sqrt{e}$ can be taken as an approximation where e is the gross (hydraulic horsepower/brake horsepower) pump efficiency. Efficiencies of pump designs running as turbines are usually 5 to 10 efficiency points lower than those as pumps at the best efficiency point.

OPERATING BEHAVIOR

By considering the flow as stopped but the turbine casing full of liquid, it is intuitively obvious that to rotate the wheel or impeller in either direction power will have to be put in. As the flow increases

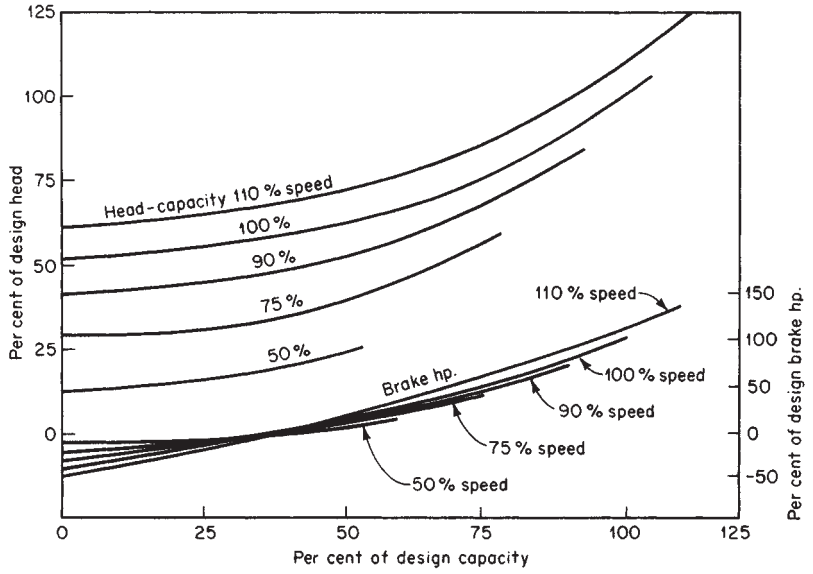


FIG. 29-52 Generalized curves showing hydraulic behavior of centrifugal pumps operating as power-recovery turbines.

from the no-flow conditions, the fluid velocity through the wheel gradually approaches such a rate that it imparts enough energy to the wheel not only to overcome internal friction but also to permit some net power output for consumption; this point usually occurs at about 30 to 40 percent of design flow or capacity. As in any turbine driver, the machine will speed up until the load imposed on the shaft coupling by the driven unit equals the power entering from the power-recovery wheel. Like a pump, a power-recovery unit will ride its characteristic curve and seek a point at which its particular head-capacity-speed-power-output relationship is satisfied. In most applications, the head available to the unit, being largely composed of a static-pressure difference, is nearly constant and varies only to the extent that inlet and exit piping-friction losses vary with flow through the unit. Thus the unit finally acts as an orifice in a relatively fixed differential system, meaning that it has a definite flow limit which also produces a torque and horsepower limit. This can be seen by following the 100 percent head curve of Fig. 29-52.

Performance Characteristics Performance of the power-recovery unit **operating as the sole driver** (Fig. 29-54) is shown in Fig. 29-55. If it is assumed that more liquid at the available head is presented to the power-recovery unit than is needed to generate the horsepower required by the pump, the turbine unit will speed up to handle the liquid, and at the same time the pump speed must go up. In speeding up, the turbine will generate more horsepower, which the pump must absorb while it is at the new speed. Finally, a balance point on horsepower is reached with the driven unit, but the number of revolutions per minute may be off design. If speed control of the driven unit is necessary, throttling some of the available capacity across a valve bypassing the unit permits the unit to satisfy its horsepower-capacity-speed relationship at the desired number of revolutions. A similar problem occurs when the capacity available to the unit is less than that needed at available head and design revolutions. The unit will slow down, try shedding load, and attempt to come to peace with its head-capacity-speed curve sets. Here speed control can be achieved by throttling the available pressure so that the unit sees only that portion of the available head needed to satisfy its head-capacity-speed relationship at the desired number of revolutions.

Performance of the power-recovery unit **operating with a makeup driver** (Fig. 29-56) is shown in Fig. 29-57; specific percentage values are shown, but the general characteristics and curve shapes are typical. It should be noted that the flow scheme, the selection of equipment, and the design of that equipment have produced the relatively inflexible system pattern shown in the curves, in which (1) except at a single point the recovery unit always requires either flow bypassing or inlet-pressure throttling (see bottommost curve); and (2) the horsepower output of the recovery unit is reduced at any point away from design (note the horsepower-difference curve), which, combined with the characteristics of steam turbines, produces the unusual turbine throttle steam-flow curve (second from the top in Fig. 29-57).

DESIGN CONSIDERATIONS

Involved in producing the curves for Figs. 29-53 and 29-55 is a calculation of the so-called **balance point** at which the flow and revolutions per minute required by the recovery unit match those provided by the pump. If the recovery turbine is the sole driver (as for the lean pump of Fig. 29-54), both the speed and the brake horsepower of the recovery turbine and its driven pump must be the same at the so-called balance point. If there is a makeup driver and the recovery unit has available to it just the flow from the pump that it is driving, as for the pump of Fig. 29-56, then the speed and capacity must match at the balance point.

Example 2: Units for a Power Recovery System The scheme of Fig. 29-52 and the actual units supplied (Figs. 29-58 and 29-59) will be used for purposes of illustration. Since this case has the recovery unit as the sole driver, the balance point is set by speed and horsepower.

For purposes of example, assume a flow of 8.71 m^3/min (2300 gal/min) through the tower. The maximum head available to the recovery turbine was calculated to be 604 m (1982 ft); this value will be slightly in error when part of the flow is bypassed since frictional losses into and out of the recovery unit will change. First, assume the lean pump to be at 3.03 m^3/min (800 gal/min) running at 3900 r/min with the semilean pump at 5.68 m^3/min (1500 gal/min) to get the total flow of 8.71 m^3/min (2300 gal/min). At 3.03 m^3/min (800 gal/min) and 3900 r/min the available head of the lean pump is read from the curve. This must be greater than the required head, and the excess is plotted as in Fig. 29-60. The brake horsepower of the lean pump is also read.

Now, at 3900 r/min and a head of 6.04 m (1982 ft), the required flow and generated brake horsepower of the recovery turbine are read. Since the horsepower of the lean pump and the recovery turbine are not identical, this entire process is repeated at another speed with the 3.03 m^3/min (800 gal/min). The difference in brake horsepower between the lean pump and the recovery turbine is then plotted against the speed for these two points, and a line is drawn between

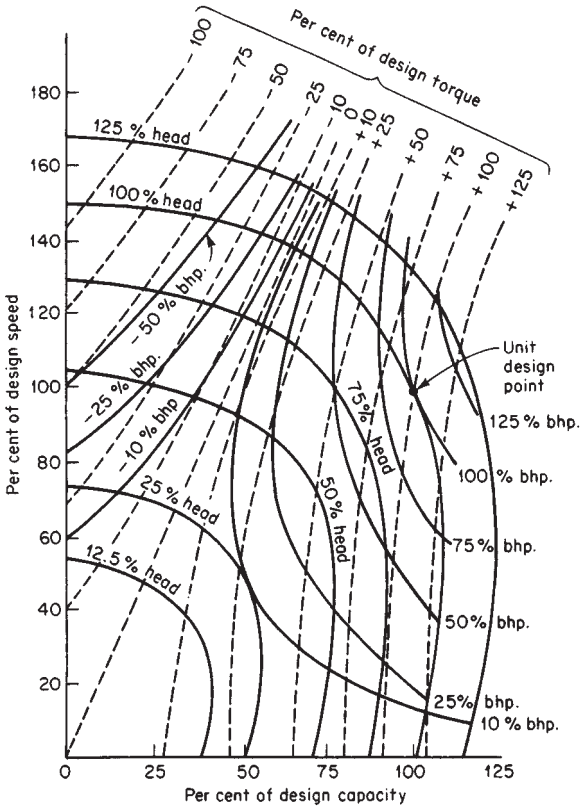


FIG. 29-53 Generalized curves for centrifugal pumps operating as power-recovery turbines.

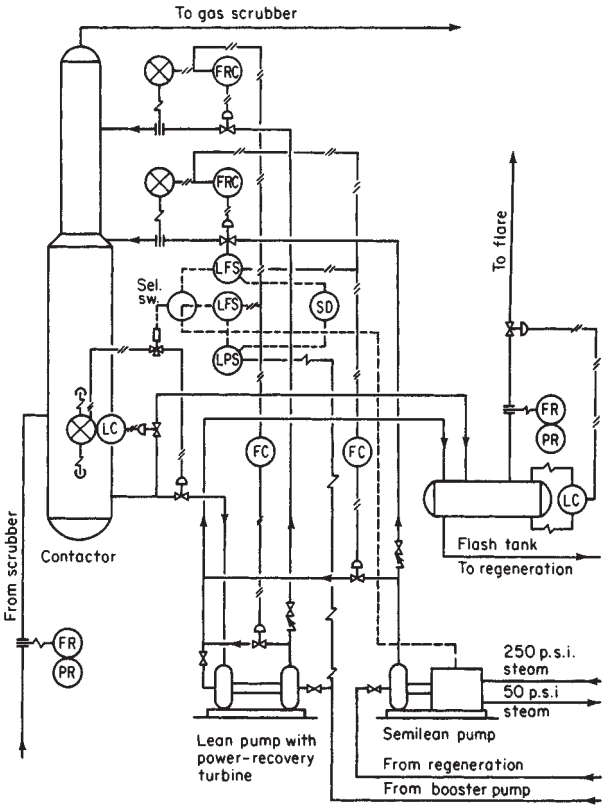


FIG. 29-54 Flow diagram of a power-recovery unit operating as the sole driver.

them. Where this line crosses the zero-difference brake-horsepower line is the balance point at 8.71 m^3/min (2300 gal/min) through the tower and 3.03 m^3/min (800 gal/min) through the lean pump.

The same procedure may be used at other pump flows to permit plotting the series of balance-point curves as has been done in Fig. 29-61. From such curves, one can establish the maximum lean pump at any total tower outflow, and combining this with the semilean-pump performance curve results in Fig. 29-55. Bypass flow plotted in Fig. 29-55 is obtained by adding simultaneous lean- and semilean-pump flows and subtracting the recovery pump-turbine flow required to make the balance point at that lean-pump flow.

Design Bases It is apparent that the balance point is always determined by the power r/min characteristics of the driven unit as sensed at the coupling by the shaft of the power-recovery pump-turbine. If the driven unit can simply soak up any (all) of the generated horsepower, for instance, a floating electric generator, then capacity control and pressure throttling may not be needed. When a speed-controlling variable-horsepower unit such as an electric motor or a steam turbine provides a tandem helper or a makeup driver, these units will hold revolutions per minute constant and make up just enough horsepower to permit the power-recovery pump-turbine to satisfy its head-capacity curve at virtually any flow rate.

It is the **combined unit characteristics** which must be considered, and these characteristics must be evaluated over the full operating range as well as for the startup condition. The consumption of power, up to almost 40 percent of design output, on starting up and coming up to speed and the fact that under a relatively fixed head condition the maximum speed at zero torque is about 140 percent of design have both already been noted. These, of course, bear particular significance for starting the unit up or shutting it down and must be considered. Failure to perform a complete system analysis can frequently lead to a process design that proves, upon installation, to be an operating trap.

In realizing the advantages of competitive designs for hydraulic power-recovery systems, there is usually an investment premium which must be paid for the **operating flexibility** illustrated in Fig. 29-55. This takes the form of additional reduced-capacity pumps and steam-turbine drivers, as well as some sacrifice in power recovery that results from bypassing or throttling even at the design point. If investment is to be minimized, a tightly designed system for full power recovery with a single pump-turbine helper, as in Fig. 29-54, may be worth considering. In such systems, the only fluid available to the pump-turbine is that provided by the pump it drives, and no separate pump with auxiliary driver is available for startup. Operating personnel will immediately see that such systems are relatively inflexible and difficult to operate (Fig. 29-57). Thus, while the tightly designed system has a minimum investment and more power recovery, it may not be the most desirable if operation away from the design point is anticipated, since only at that one point is neither throttling nor bypassing needed. Furthermore, it becomes apparent that the maximum steam requirements may be set by a partial-load condition rather than by design conditions or overload.

While the foregoing examples have dealt with applications on centrifugal pumps, the same sort of analysis can be made for reciprocating pumps, reciprocating compressors, or other rotary users like cooling-tower fans.

INSTALLATION FEATURES

In addition to performing the system analysis, a number of details or peculiarities of the units must be considered with respect to:

1. Vaporization, flashing, or cavitation
2. Fluid volumes
3. Process-stream controls
4. Speed control

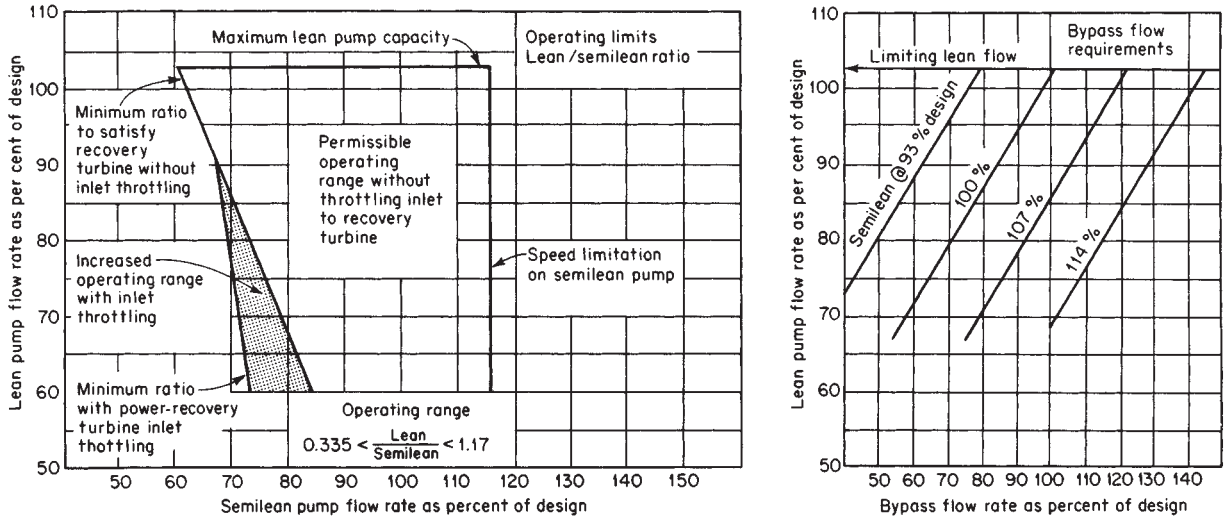


FIG. 29-55 Performance of a power-recovery unit operating as the sole driver.

5. Startup and overcapacity
6. Electrical-system characteristics if the recovered power is used to generate electricity

Vaporizing Fluids Many pump-turbines are installed on gas-saturated liquid streams, and loss in pressure can cause problems whenever this occurs across balancing drums or pressure-reducing labyrinth seals. Piping that carries bleed streams from the drums and seals to the low-pressure (outlet) side of the pump-turbine must be sized generously to allow for some gas evolution.

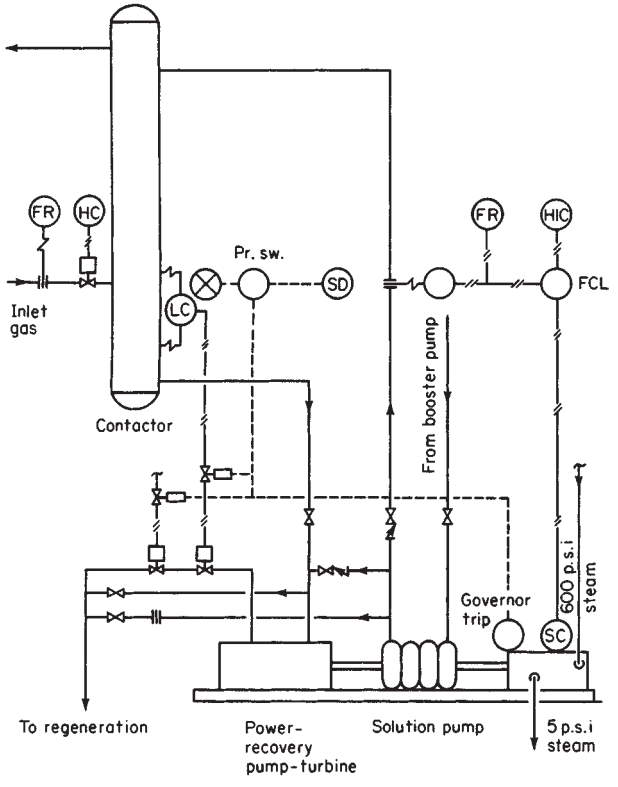


FIG. 29-56 Flow diagram of a system with a power-recovery turbine operating with a makeup driver.

In general, gas evolution is not evident in the pump-turbine's casing proper, for the corresponding added horsepower (as would be anticipated from the gas expansion) has never been evidenced in reports on field testing. It appears that the liquid passage through the casing is too fast for vapor-liquid equilibrium to be attained. However, slower shearing passage through a balancing drum and return line does permit gas evolution, and this line may become vapor-locked if it is undersized. Similarly, the high points of the pump-turbine casing may be vapor-locked with released gas if the unit stands idle; this can cause damage to seal chamber, balancing-drum chambers, etc., when the unit is started up again.

There is another potential hazard due to vaporization which does not generally occur in process-plant installations. The hazard results from the fact that a pump sees only the head of fluid, and if significant flashing occurs in the inlet piping, the head of fluid represented by the pounds-force-per-square-inch-gauge inlet pressure can be many times greater than design head, resulting in an attempt by the unit to increase its speed greatly.

There also appears to be a minimum outlet or impeller eye pressure below which cavitation and its attendant physical damage can occur (similar to net positive suction head, or NPSH, this could be called net positive discharge head, or NPDH). Thus it is often advisable to design by using only a part of the full pressure differential available in the process for the pump-turbine. If throttling is to be provided, outlet throttling is probably better than inlet throttling, and if used, any mechanical seals, as well as the unit casing outlet flange, must be adequate to withstand the full inlet pressure when the throttle valve is closed.

Fluid Volumes Many process-plant installations of these units are made by handling *rich liquid* out of an absorber. In most cases both liquid volume and liquid density will change from input to output. While such changes are not normally significant, the sensitivity of the balance point to the volume of flow makes it mandatory to consider volumetric swell by absorption in checking the suitability and adequacy of the pump-turbine unit and the controls and bypassing arrangements as part of a system analysis.

Process Controls If the inlet or outlet liquid to a pump-turbine is regulated by a level controller on the liquid-supply vessel, a falling liquid level inside the vessel will cause this controller to throttle a valve, reducing the differential pressure available to the pump-

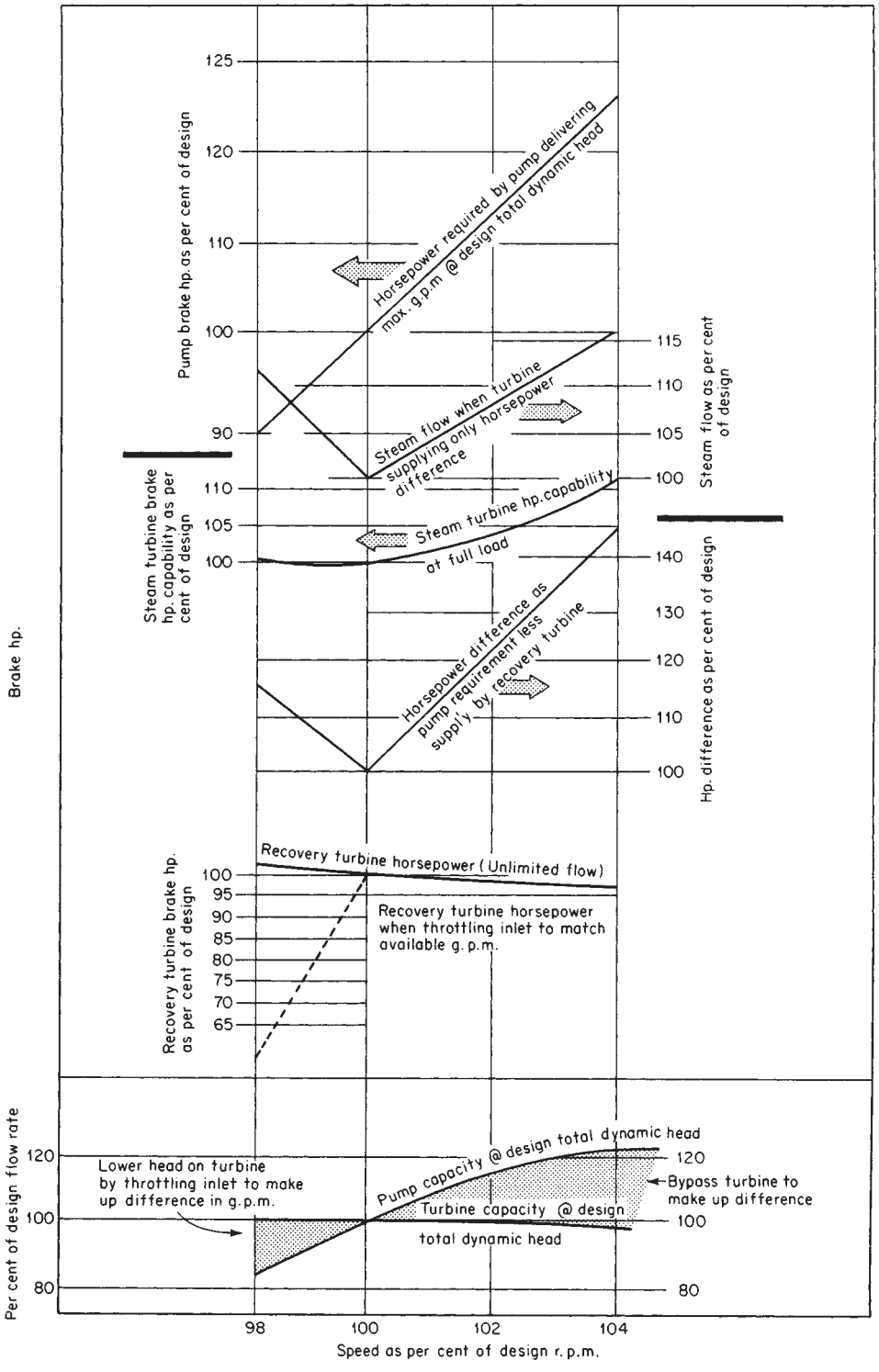


FIG. 29-57 Performance of a power-recovery turbine operating with a makeup driver.

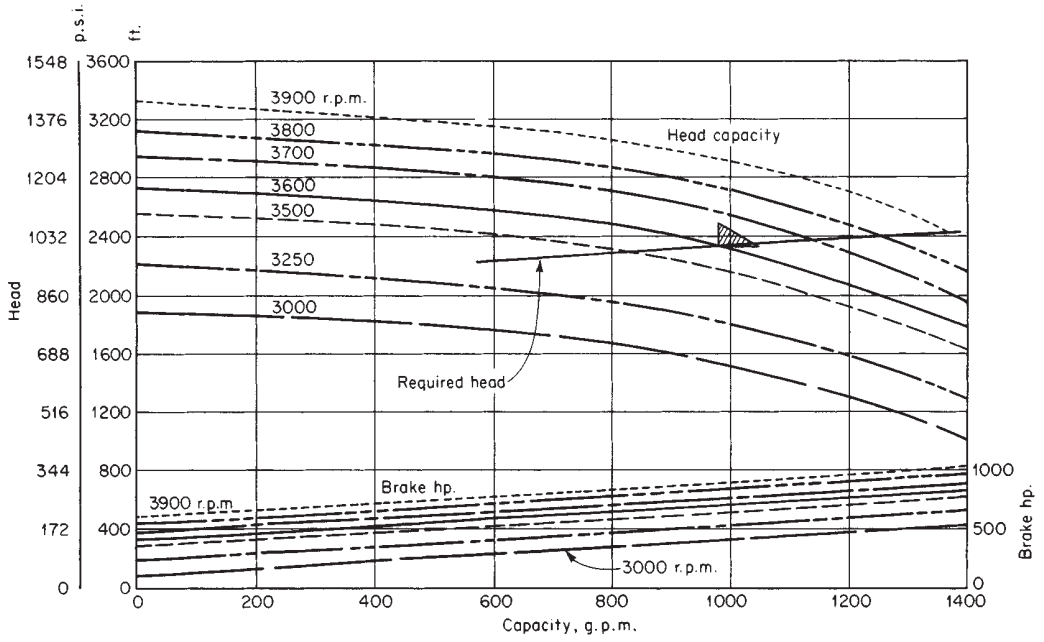


FIG. 29-58 Head-horsepower-capacity characteristics of a lean pump tandem-connected with a power-recovery turbine operating as the sole driver. To convert gallons per minute to cubic meters per minute, multiply by 3.79×10^{-3}; to convert horsepower to kilowatts, multiply by 0.746; and to convert pounds-force per square inch to megapascals, multiply by 6.89×10^{-3}.

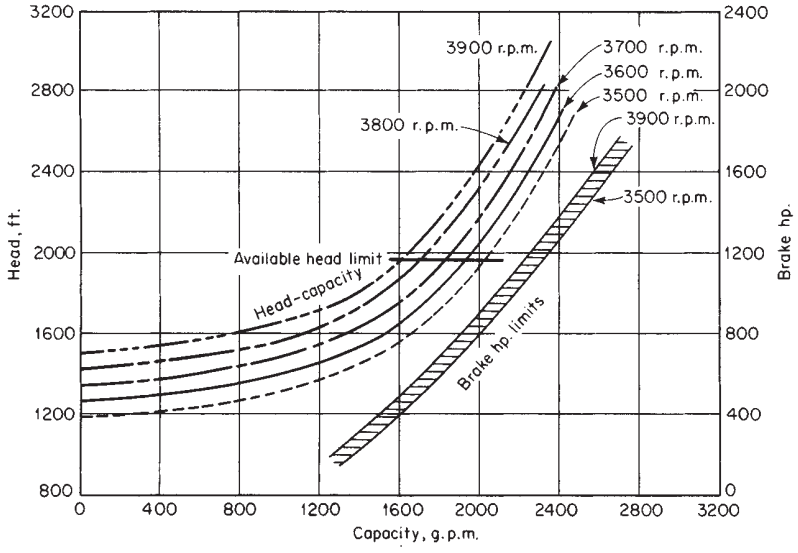


FIG. 29-59 Head-horsepower-capacity characteristics of a power-recovery turbine operating as the sole driver of a lean pump. If the total capacity of lean and semilean pumps exceeds the values indicated by "available head limit," bypass must be used. Net recovery-pump head at 8.71 m^3/min (2300 gal/min) is figured as follows:

Tower	957 lbf/in^2	6.598 MPa
Flash tank	–75	–0.517
Suction piping (62.4 lb/ft^3)		
Friction loss	–11.8	–0.081
Elevation	+2.8	+0.019
Discharge piping (57.8 lb/ft^3)		
Friction loss	–8.8	–0.061
Elevation	–5.6	–0.038

To convert gallons per minute to cubic meters per minute, multiply by 3.79×10^{-3}; to convert horsepower to kilowatts, multiply by 0.746; and to convert pounds-force per square inch to megapascals, multiply by 6.89×10^{-3}.

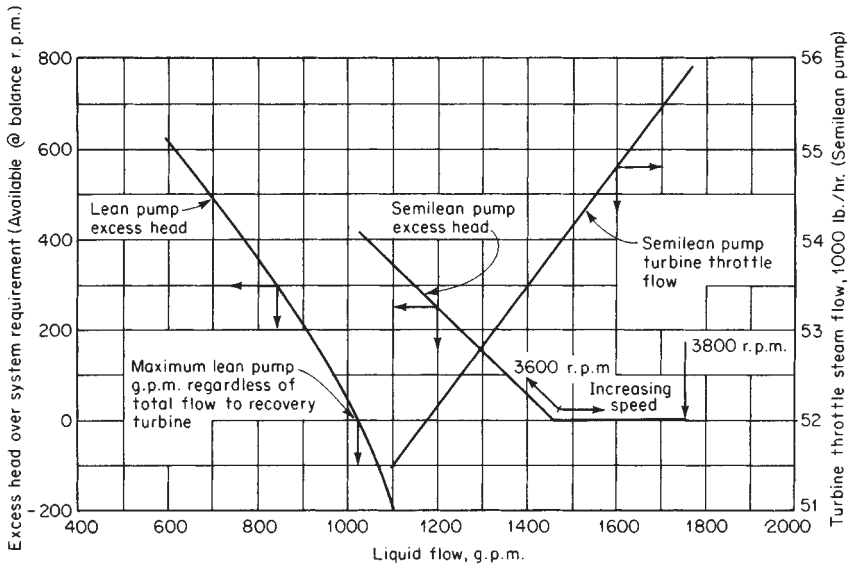


FIG. 29-60 Excess head developed by lean and semilean pumps and the steam-throttle flow for a semilean-pump turbine. To convert gallons per minute to cubic meters per minute, multiply by 0.00379; to convert pounds per hour to kilograms per second, multiply by 1.260×10^{-4}.

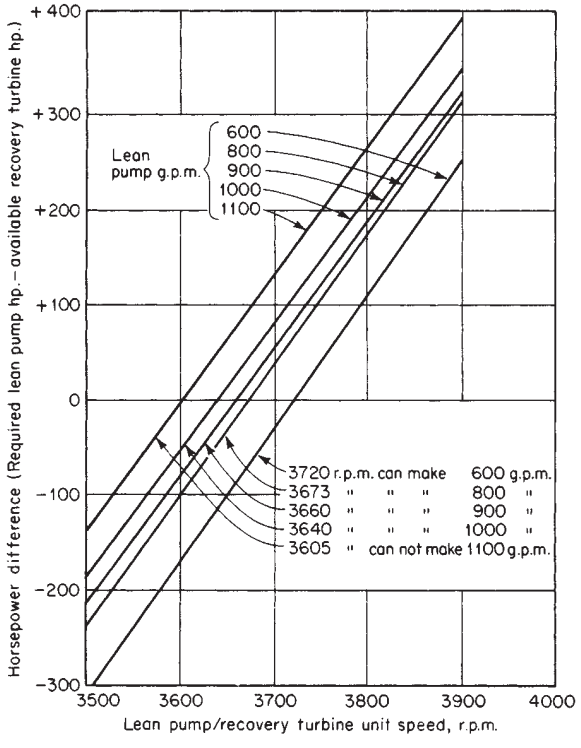


FIG. 29-61 Horsepower–r/min balance for a lean pump tandem-connected with a power-recovery turbine operating as the sole driver. Horsepower differences are calculated from excess head requirements as typically shown in Fig. 29-60. To convert gallons per minute to cubic meters per hour, multiply by 0.2271; to convert horsepower to kilowatts, multiply by 0.746.

turbine; or if the liquid level is rising, the control valve tends to open wide, so that the pump-turbine sees its full available head. Since under this latter condition the head is at its maximum, no more liquid will flow through the pump, and if the level continues to rise, the system goes off level control. One performance like this inevitably leads to a request from operating personnel for a bypass around the pump-turbine. On a startup it is frequently necessary to have a bypass from a point upstream of the driven pump's discharge check and block valves to the associated pump-turbine.

Speed Speed control can be critical with pump-turbines. Considering the characteristics shown in Fig. 29-57 (and the curves on which it is based), a 4 percent change in speed, from 98 to 102 percent, produces a 33 percent change in pump flow, from 82 to 115 percent, and about a 22 percent horsepower change, from 118 to 100 to 122 percent. A NEMA Class A steam-turbine mechanical governor has about 10 percent steady-state regulation, so that for the 22 percent horsepower speed change one should not expect better than a 2 percent speed regulation. Since 4 percent is the total speed change being considered, it becomes apparent that a problem exists in governing the speed of the steam turbine. Since this unit is supposed to serve to hold pump speed by supplying horsepower as needed to get a match of pump and system curves at the desired flow rate, this is a serious concern. In this case the problem can be solved by eliminating the steam-turbine speed governor, leaving only the overspeed trip, and placing a control valve actuated directly by pump-flow measurement in the steam-supply line to the turbine.

In contrast to steam turbines, in which runaway overspeeding is always a problem, pump-turbines operating at design head go to zero torque at about 130 to 140 percent of design speed. Thus, overspeed protection may not be necessary if the pump-turbine can withstand 140 to 150 percent of design speed and it is the sole driver. When a steam-turbine helper is used, it should be provided with the usual overspeed trip-out mechanism.

Startup and Overcapacity From a design standpoint and also operationally, it is important to remember that pump-turbines not only do not generate power before they attain about 40 percent of design flow but actually consume power in decreasing amounts as the flow is increased from zero to 40 percent. This means that they should

be brought up to operating speed as rapidly as possible. Another solution, and a more desirable one from an operating and maintenance standpoint, is to install a free-wheeling or overriding clutch (such as that made by the Marland Division of Zurn Industries, Inc., of La Grange, Illinois) between the turbine and the pump. With such an installation, the pump does not have to turn until fluid is available to it. Also, it is not connected to the pump until it tries running faster than the pump, at which time it is putting out power. Under this arrangement the startup sequence can be selected so that the turbine unit goes from zero speed to operating speed along the zero-torque curve.

At design head, on the other hand, capacity does not change markedly with speed, so that once the design point has been passed the pump-turbine acts as a restriction in the line. Since most of these units operate on a relatively fixed pressure differential, they then tend to act like an orifice to limit flow, and little or no benefit can be realized from any overcapacity in terms of fluid flow available to the unit in the actual installation.

Electrical Generation When pump-turbines are used to generate electricity, the units should be tied into electrically strong networks of such a size that the pump-turbines cannot swing the system frequency but are governed by that frequency and become constant-speed machines. Inlet or outlet throttling, as well as bypassing, must be used for such installations. Consequently, with speed fixed and available head essentially constant because of the process, the maximum amount of recoverable power is established by the design. Once installed, a pump-turbine cannot be pushed into generating more power if more fluid is available except by a redesign of its internals. The electrical portion of such an installation is straightforward, controls are simply inlet throttling and a bypass (if needed) for the pump-turbine, and these controls can be operated on a split range from the same level controller on the liquid-source vessel.

Integral Units A relatively recent development is the integral or packaged pump-turbine unit assembled in a single casing, having a common discharge port and designed for mounting directly in the piping. A cutaway view of one such design is shown in Fig. 29-62. It is obvious that the use of such a unit presupposes the compatibility and desirability of having the pump discharge material contaminated by all the powering fluid which passed through the driving turbine impeller. So far, this unit has seen little service in process plants, but its simplicity, its independence of normal power sources, and its ease of installation make it an attractive candidate for consideration when the process-flow-scheme can be adapted to its characteristics. It has been proposed for use in place of liquid eductors or ejectors, for it has a much higher efficiency than such units, and furthermore throttling motive fluid flow will cause the pumped fluid flow to follow according to balance-point requirements.

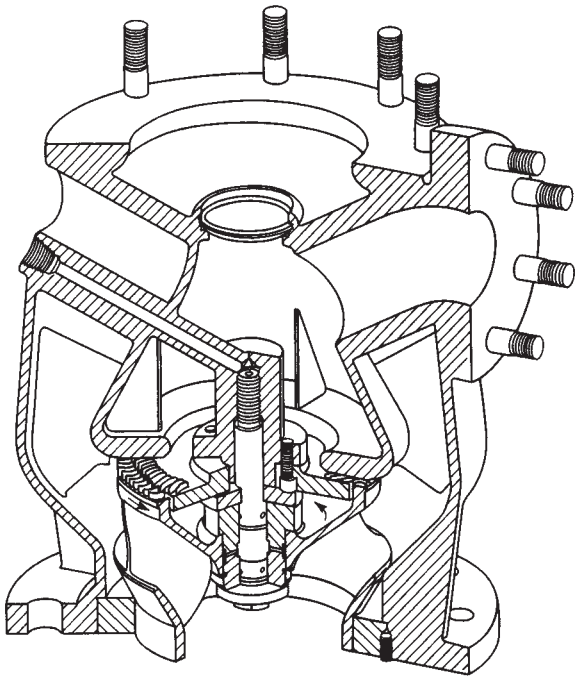


FIG. 29-62 Integral or packaged pump-turbine unit. (*Worthington Division, Dresser-Rand Co.*)

MECHANICAL POWER TRANSMISSION

Process machinery usually involves a driver and a driven machine, and these machines are connected by power-transmission equipment. Such equipment can either be mechanical or hydraulic.

For instance, power can be transmitted from one machine to the other through shafts, flexible couplings, and gear reducers (mechanical equipment). Power can be transmitted through a torque converter (hydraulic equipment) or by a combination of mechanical and hydraulic equipment.

Although power-transmission equipment is generally simpler than the machines it connects, it nevertheless fails in service as often as—if not more often than—motors, turbines, pumps, and the like. Care must be given to the proper selection and maintenance of power-transmission equipment; otherwise, the best process machines cannot perform as expected.

This segment will discuss the more commonly used power-transmission equipment; also discussed will be the machinery bearings, which not only support the rotors of machinery, but the power-transmission equipment as well.

The segment is divided into the following parts:

- Bearings
- Power transmission without speed change
- Power transmission with change in speed
- Lubrication of power transmission equipment

BEARINGS

Rotating shafts must be supported by the machine housing, not only against gravity, but also against a variety of forces that are imposed on rotors inside machines (including axial thrust). Bearings have a significant influence on the performance of process machines, both because they limit their continuous operation and also since they influence the level of vibration and critical speeds of the machines.

It was generally accepted that "machinery users do not select bearings" (see the sixth edition of this handbook); this is no longer valid: users have realized that they can have a voice in the selection of bearings of new machines and that they can select better bearings for their old machines than the ones supplied by the original equipment manufacturer (OEM). A number of independent bearing manufacturers can be found in most industrial areas.

Until quite recently, all types of bearings required lubrication; the advent of magnetic bearings has eliminated the need for lubrication. Lubricated bearings have a significant power loss, as oils or greases are sheared by the relative motions between shafts and housings; magnetic bearings eliminate the losses in lubricants, but they require electrical power to maintain the shaft journals in the desired position.

Three types of bearings will be discussed: oil-film bearings, rolling-element bearings (also known as antifriction bearings), and magnetic bearings.

Oil-Film Bearings The name *oil-film bearing* derives from the fact that, in such bearings, shafts are supported by a film of oil under significant pressure. This pressure is generated by the rotation of the shaft and by the fact that the clearance between the shaft and its bearing has a wedge shape. A typical radial oil-film bearing is illustrated in Fig. 29-63. The bearing has a diametrically split shell, having a layer of low-friction material (babbitt) on the inside surface. The outside diameter fits tightly in the machine housing, and an antirotation pin (or protrusion) is provided. This pin also serves the purpose of axially locating the bearing. Between the inside surface of the bearing and the shaft journal, there is a clearance filled with oil under a pressure of about 20 psi (1.4 bar, 138 kilopascals).

This clearance is very important for bearing and machine performance. A too-tight clearance will allow very little oil to flow through the bearing, which will operate hot; a too-loose clearance will prevent the formation of a high-pressure film of oil, and the bearing will fail through mechanical contact. It is customary to use the following clearances:

- For low to moderate speeds, $0.001 \times d + 0.002$ (inches)
  $0.001 \times d + 0.05$ (mm)
- For high speeds, $0.002 \times d$

where d is the journal diameter.

The clearance in oil-film bearings is necessary for the formation of a film of oil; however, it is detrimental because it allows shafts to vibrate within. Machinery vibrations tend to appear with wear and with the unbalance created by blade fouling. In many cases, machines can be made less sensitive to vibrations by changes in bearing design; there are types of oil-film bearings that resist shaft motions without decreasing the internal clearances. To understand how such bearings work, an explanation of *preload* is in order.

The normal operating position of a shaft inside a bearing is shown in Fig. 29-64. It can be seen that, due to radial forces, the geometric center of the shaft does not coincide with the one of the bearing. This displacement creates a "wedge," which combined with the shaft motion, forces the oil into a continuously decreasing area, and a hydraulic pressure is generated. This pressure acts on the journal and supports it against gravity or other internal forces. To stabilize a vibrating shaft, bearings with larger oil pressures are used. A larger pressure is created whenever the shaft moves closer to the bearing (steeper wedge), which is not desirable. Therefore, an "apparent" proximity is created by altering the geometry of the bearing.

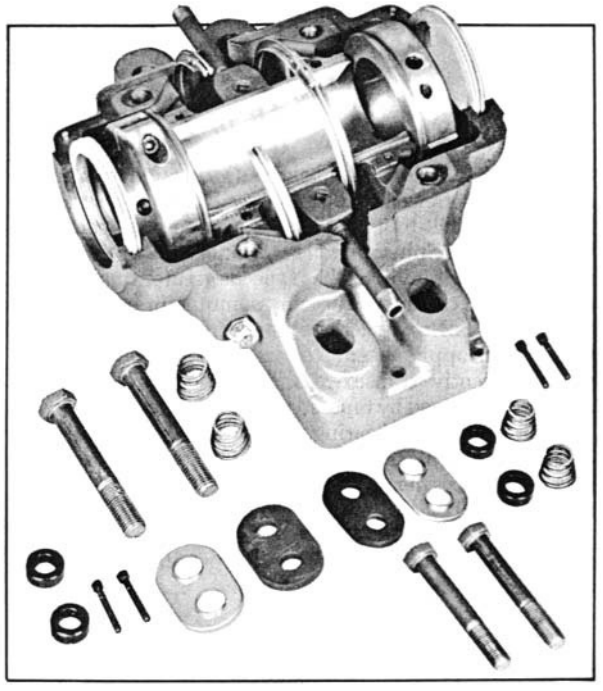


FIG. 29-63 Typical oil-film pillow-block bearing. Lubrication is provided both by an oil flow and by oil rings.

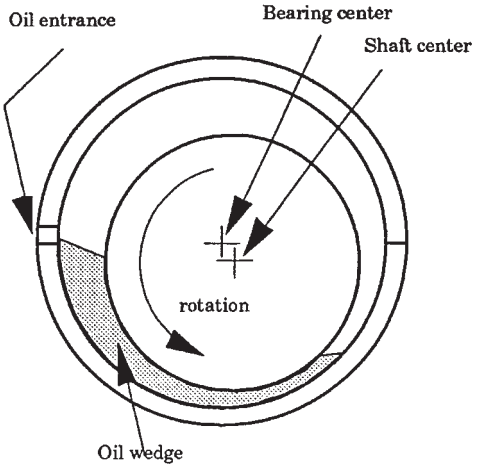


FIG. 29-64 Operation of oil-film radial bearings.

A lemon-bore bearing configuration is shown in Figure 29-65. It can be seen that a steep wedge was generated by *apparently* making the bearing diameter larger; this is similar to a normal bearing with a larger load; therefore, these types of bearings are known as preloaded bearings. *Preload* in this case does not refer to forces but rather to the resulting geometry.

Another way to stabilize a shaft inside a bearing is to use "pressure-dam" designs, as shown in Fig. 29-66. The oil supply pressure is directed to the top of the shaft; it forces the shaft downwards, and it stabilizes its motions.

The most modern oil-film bearings use movable pads, which tilt in order to create, automatically, the optimum wedge shape. They are known as the "tilting pad" bearings and are illustrated in Fig. 29-67.

Oil-film bearings are also used for positioning shafts axially, against thrusts created by the flow of the processed fluid through machines.

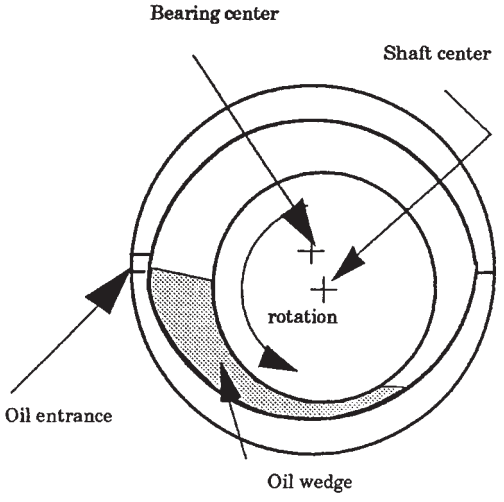


FIG. 29-65 Oil-film bearing with geometrically-created preload.

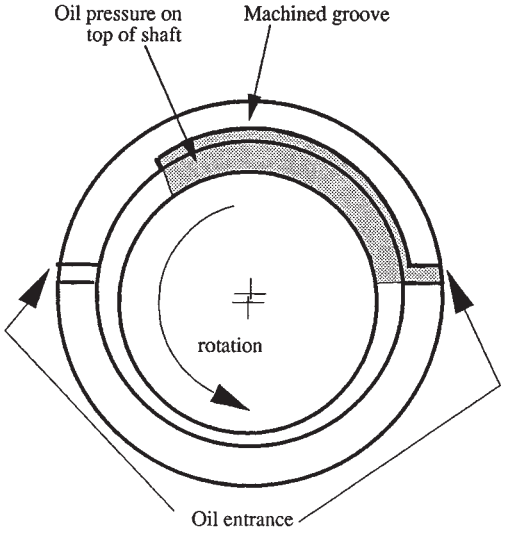


FIG. 29-66 Oil-film bearing with oil pressure created preload (pressure dam design).

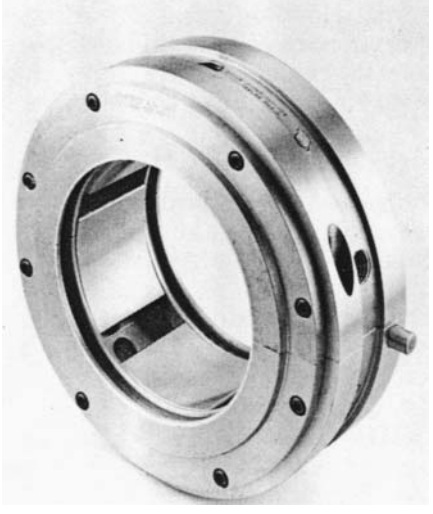


FIG. 29-67 Radial oil-film bearing with tilting pads.

Thrust bearings have an active side, against which the bearing collar or disc is forced; they also have an inactive side, which has the purpose of limiting the total axial float of a rotor, should the thrust reverse for any reason. Just as radial bearings require a clearance between the journal and the bearing, so do thrust bearings require a float of the thrust disc between the two sides of the bearing. A typical oil-film thrust bearing is illustrated in Fig. 29-68. Thrust bearings, just as radial bearings, can have a fixed geometry or can be equipped with tilting pads.

Rolling-Element Bearings With this type of bearing, shafts are supported by small parts that roll with no friction, at least theoretically. The rolling elements can be spherical (ball bearings), cylindrical (roller and needle bearings), or conical (tapered roller bearings). Although more complicated than fluid-film bearings, rolling-element bearings are less costly, mainly because they are manufactured in very large quantities. Their main disadvantage is a limitation in maximum operating speed. The main types of rolling-element bearings are shown in Fig. 29-69.

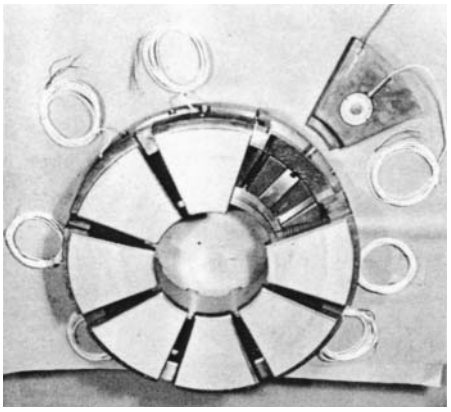


FIG. 29-68 Axial (thrust) oil-film bearing with tilting pads and embedded temperature sensors.

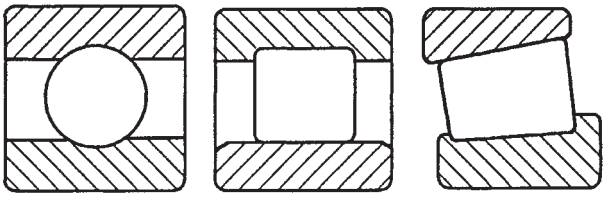


FIG. 29-69 Three types of rolling-element bearings: ball, cylindrical roller, and tapered roller.

Generally, the rolling elements ride on an internal race, installed on the shaft, and an external race, installed in the machine housing. The races and the rolling elements are made of hardened alloy steels, because the contact pressure caused by the radial (or thrust) forces can be very high.

The rolling elements are installed in a cage that performs the very important role of reducing the friction inside bearings. The conditions without a cage are shown in Fig. 29-70. It can be demonstrated that the rotational speed of a rolling element around its geometric center is:

$$\text{rpm}_1 = \frac{\text{rpm}_2}{2} \times \frac{R}{r}$$

For example, if the inner race diameter is 4 in and the balls have a diameter of ⅜ in, the balls will rotate 5.3 times faster than the shaft. If balls touch, then the relative velocity occurs at twice their revolution, and the friction so generated will overheat the bearing. Depending on the rated speed of a bearing, cages are made (in increasing order of speed) of steel, phenolics, or bronze. Brass and polymers are also used.

Rolling-element bearings require lubrication for minimizing the friction between the rolling elements and their cage and for dissipat-

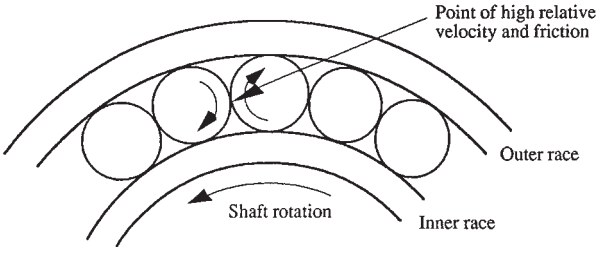


FIG. 29-70 Cageless roller bearings would operate hot and wear rapidly.

ing the heat generated by friction. Depending on the operating speed, lubrication can be provided by greases, liquid oil, or oil mist.

The selection of rolling-element bearings is based on the radial and axial loads they must support, on the operating speed, and on the expected life. All bearing catalogs provide comprehensive selection data.

Rolling-element bearings are provided with a small radial clearance that almost disappears when they are pressed on the shaft or in the housing. Basically, a rolling element bearing is pressed on its shaft and has a small clearance in the housing when the shaft rotates and the housing is stationary; the reverse is true when the housing rotates, as is the case for idler pulleys.

Magnetic Bearings Magnetic bearings replace the hydrodynamic shaft support by a magnetic field. Their advantages and disadvantages are summarized in Fig. 29-71. While oil-film bearings create the necessary power to support the shaft from the movement of the shaft, magnetic bearings need an outside power supply. A magnetic bearing system consists of four major components: magnetic actuators, power supply, shaft-positioning sensors, and electronic controls. Magnetic forces act all around the shaft; sensors detect the relative position between the shaft and the housing and send the signals to the controller, which supplies more or less electrical power to the electromagnets so that the shaft remains centered independent of the forces acting on it. The principle of operation of a magnetic bearing is shown in Fig. 29-72.

Because magnetic bearings do not require lubrication, they are particularly suited to applications such as canned pumps, vacuum pumps, turbo-expanders, and some centrifuges. As of 1994, some centrifugal compressors in the 5000-kW power range had been equipped with magnetic bearings.

The rotordynamic study of a machine with magnetic bearings is quite different from the one of either oil-film or rolling-element bearings. The stiffness and damping properties of magnetic bearings can be adjusted (within limits) by altering the feedback and response time between the sensors and the electromagnets.

Advantages	Disadvantages
Low power usage	Small load capacity
Very long life	Large size
No Oil required	Higher investment
Low *system* weight	Requires mechanical backup
Reduced fire hazard	for power interruptions
Vibration sensors built-in	New technology
	Possible rotor-dynamic problems

FIG. 29-71 Advantages and disadvantages of magnetic bearings.

POWER TRANSMISSION WITHOUT SPEED CHANGE

Whenever the process machine operates at the same speed as its driver, the two can be directly coupled. This direct coupling still allows for a variable speed, through adjustments of the speed of the driver. Steam turbine speed can be easily adjusted, and electric motor speed can also be varied by the use of special drives that vary the *frequency* of the power applied to the motor. Whether the speed is fixed or variable, direct coupling of two machine shafts presents the problem of accommodation of misalignment. To this purpose, machines are coupled through a *flexible coupling.*

Variable-Speed Electric Motor Drives Whether of the induction or synchronous type, ac motor speed is a direct function of the supply voltage frequency. The advent of high-power solid-state controllers made possible the manufacture of frequency converters. These converters can generate high power (over 14,000 kW) at a variable frequency, which can be lower or higher than the standard 60 Hz (cycles/second). Frequency converters made possible not only variable-speed motors but also high-speed (up to 10,000 rpm) electric motors. The cost of these converters is often higher than the cost of a gear unit, but the elimination of gear units makes machines simpler and more reliable.

Although motors and controllers can be bought separately, the trend is to purchase a system from a given manufacturer. There are six types of variable-speed drives, as shown in Fig. 29-73. Dynamic response indicates the ability of the drive to respond to a change in command; it is measured in radians/second; the higher the number, the faster the drive response.

Variable-Speed Mechanical Drives Although rather common until the late 1960s, mechanical variable-speed drives, Figs. 29-74 and 29-75, are seldom used today. Their relative complexity makes these drives more maintenance-prone than the newer variable-frequency electric motor drive systems. However, variable-speed fluid drives (Fig. 29-76) are finding widespread use in major machinery drives demanding precise speed control in applications ranging to 50 MW and even higher. These variable-speed turbo couplings can be combined with one or more gear stages in a common housing. The bottom part of this compact unit forms an oil sump. From the basic concept consisting of a speed-increasing gear followed by a variable-speed turbo coupling, other models have been derived to provide stepless speed control for both high-power, high-speed machines such as boiler feed pumps and compressors; and low-speed machines with a speed-reducing gear such as coal mills, ID fans, and crude oil pumps.

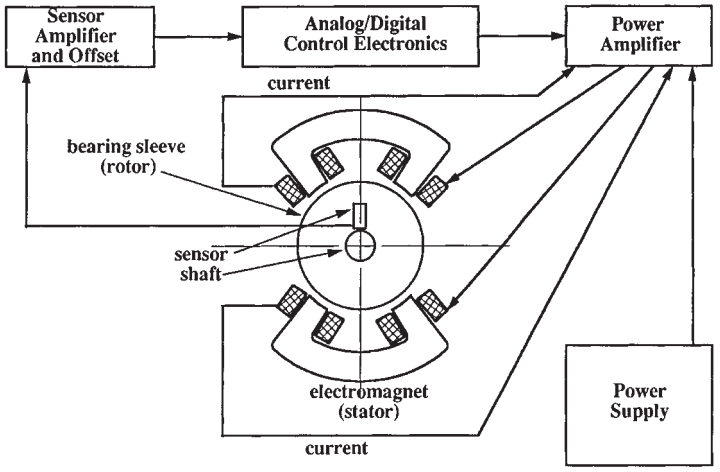


FIG. 29-72 Principle of operation of magnetic bearings.

Type of Drive	Speed Range	Starting Torque	Maximum Speed	Dynamic Response
Thyristor dc	100:1	150%	3000	15
Brushless dc	100:1	150%	3000	15
Std. Inverter	10:1	100%	6000	5
Vector Inverter	100:1	150%	6000	50
Servo	2000:1	200%	6000	500
Switched Reluctance	100:1	150%	10,000	50

FIG. 29-73 Main characteristics of typical electric adjustable-speed drives. (*Source: Reliance Electric Co.*)

The power developed by the prime mover is converted into kinetic energy in the impeller (primary wheel) of the turbo coupling and converted back into mechanical energy in the turbine wheel (secondary wheel), which is connected to the driven machine. As there is no metal-to-metal contact between primary and secondary wheels, there is no wear. Hydraulic oils with additives are used for power transmission. The amount of oil in the coupling can be varied during operation using the scoop tube. This in turn regulates the power-transmitting capability of the coupling and provides stepless speed control dependent on the load of the driven machine.

The coupling has a regulating range of 4:1 to 5:1 for driven machines with increasing parabolic torque load characteristics such as centrifugal pumps and fans. For machines with approximately constant torque load characteristics, the regulating range is 3:1. With centrifugal machines, this method of speed regulation is much more efficient than throttling the machine output, giving considerable power savings. The motor is started under no-load conditions with the coupling drained. When running the load, the motor can be controlled by the coupling. Moreover, by draining the fluid coupling, the prime mover can be disconnected from the driven machine while the prime mover is still running.

A mechanically driven oil pump on the primary side of the coupling pumps oil from the reservoir underneath the coupling through a control valve into the working chamber of the turbo coupling. The level of the oil in the working chamber and therefore the power that the turbo coupling can transmit depends on the radial position of the adjustable sliding scoop tube. The scoop tube can pick up more oil than the pump can deliver. The oil picked up by the scoop tube passes through an oil cooler/heat exchanger and control valve back to the working chamber and/or the oil reservoir. The heat exchanger dissipates the heat originating from the slip of the turbo coupling. The scoop tube actuator can be operated either electrically, hydraulically, or pneumatically.

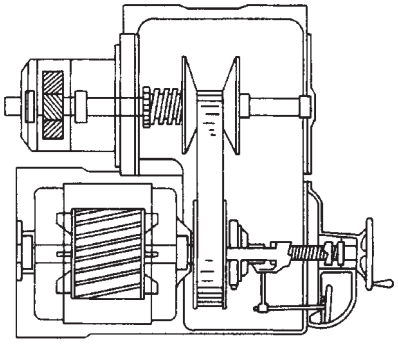


FIG. 29-75 Combined variable-speed and motor drive. (*Reeves Pulley Co.; from Kent,* Mechanical Engineers' Handbook, *12th ed., Wiley, New York, 1961.*)

Synchro-Self-Shifting ("SSS") Clutches The automatic freewheel action of an SSS clutch simplifies plant startup and shutdown sequences. It is, of course, receiving its power input from a gas turbine or similar driver, while its output is connected to a driven machine. The drive disengages automatically when the driven machine speed exceeds that of the driver. Since large gas turbines are usually brought up to speed with either a startup gear motor or a helper turbine, thousands of SSS clutches (Fig. 29-77) are finding application here.

Upon unit startup, the turning gear motor can continue to rotate

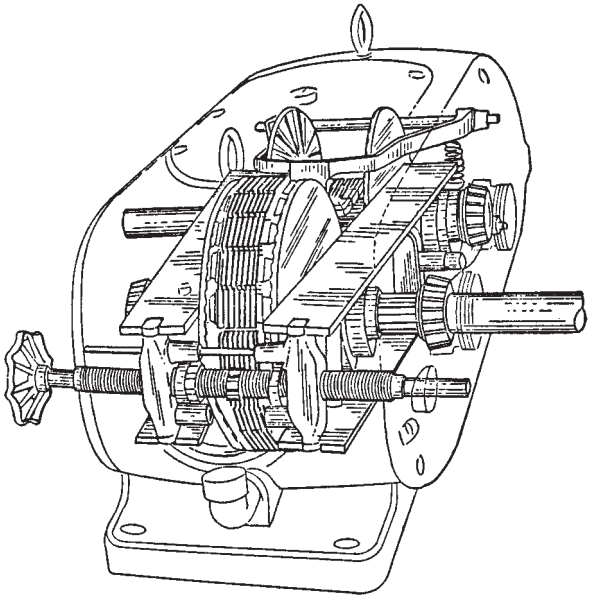


FIG. 29-74 PIV speed changer. (*From Kent,* Mechanical Engineers' Handbook, *12th ed., Wiley, New York, 1961.*)

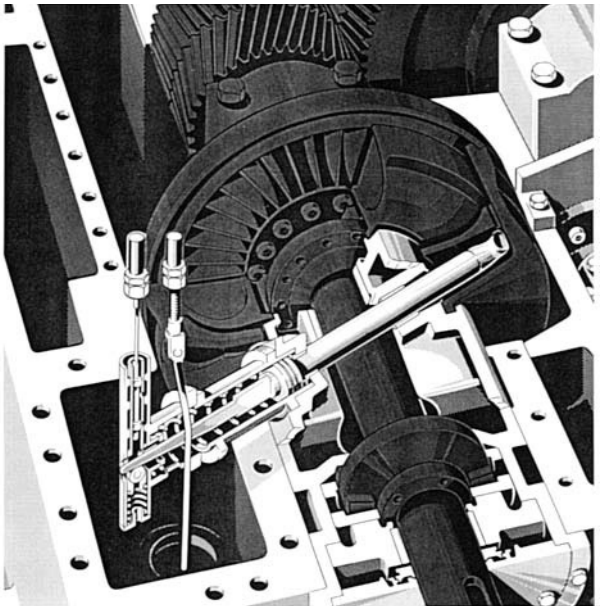


FIG. 29-76 Variable-speed turbo coupling (hydrodynamic fluid coupling). (*Courtesy of Voith Transmissions, Inc., York, Pennsylvania and Heidenheim, Germany.*)

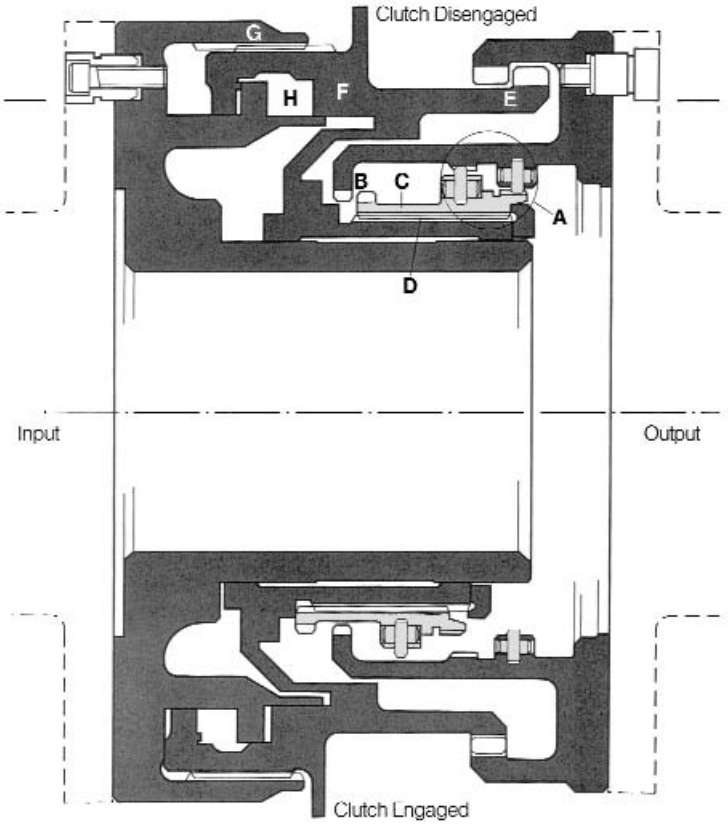


FIG. 29-77 Synchro-self-shifting clutch for large turbogenerator applications. (*Courtesy SSS Clutch Company, Inc., New Castle, Delaware.*)

or be stopped at any time. Similarly, it can be started at any time during the shutdown sequence, but the drive will only engage at turning gear speed.

Considerably larger units, with power ratings in the 300-MW range, are often fitted between a gas turbine driver and a utility power generator. This mode of application allows the generator to be used for voltage control/synchronous condensing with the gas turbine at rest but readily "on call" for peak load generation duty.

The sequence of clutch-engaging action is depicted in Fig. 29-77. Primary or secondary pawls (A) initiate engagement at clutch synchronism by aligning and engaging the relay clutch teeth (B). As the lightweight relay clutch (C) slides along its helical splines (D), the pawls are unloaded.

Primary pawls operate at low generator speeds. Secondary pawls operate at high turbine speeds. Therefore, all pawls are inert during synchronous condensing and when the clutch is engaged during power generation.

The relay clutch teeth (B) align and initiate engagement of the main clutch teeth (E). As the main clutch (F) slides along its helical splines (G), the relay clutch is unloaded.

When the main clutch teeth (E) are fully engaged, power is transmitted from the turbine to the generator. Engagement and disengagement of the main clutch is cushioned by the oil dashpot (H).

Flexible Couplings Whenever two machine shafts in substantial alignment are directly coupled, a flexible coupling is used to transmit the torque and accommodate the inevitable misalignment. A number of reasons make misalignment inevitable: thermal growth of machine housings and shafts, piping strain, foundation settlement, and so on. Without the ability to accommodate misalignment, machine shafts would fatigue and fail. Couplings accommodate misalignment either through sliding of one component over another or through flexing one or more of their components. As sliding requires lubrication, it is customary to categorize couplings as either lubricated or dry.

The most popular lubricated couplings in process machinery are the gear type (Fig. 29-78) and the grid coupling (Fig. 29-79). Lubricated couplings have the advantage of small size and weight but the disadvantage that machines must be stopped for the couplings to be relubricated (most machinery can be relubricated while running). Gear-type couplings also have the unique advantage that they can accommodate *any* axial shaft motions that machines require.

Dry couplings are divided into metallic elements and elastomer elements. For a given torque, metallic elements (disks and diaphragms) are more compact and lighter than elastomer element couplings but are less flexible; therefore, they impose larger forces on the bearings. On the other hand, elastomer elements become quickly distorted by centrifugal forces; therefore, they cannot usually operate safely at speeds larger than standard motor speed. These couplings are shown in Figs. 29-80 and 29-81.

It is important for coupling users to understand that *all flexible couplings resist being misaligned.* Hence, good alignment reduces the forces on machine bearings and increases machine reliability. Couplings designed to accommodate *large misalignments* usually can do this to the detriment of other features, such as reduced torque transmission or increased bearing forces.

It can be said that the trend in the 1980s/1990s was the gradual

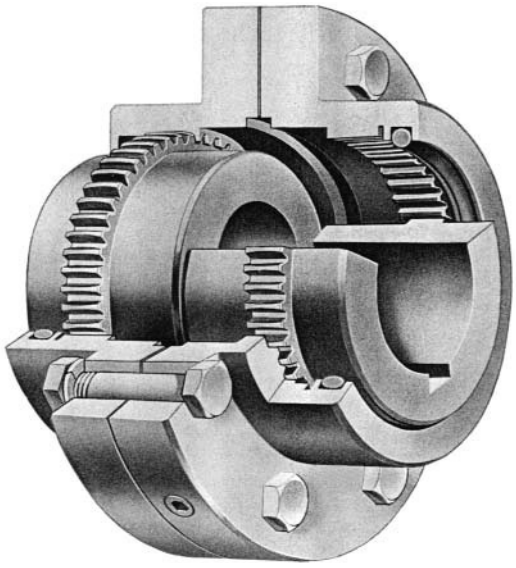


FIG. 29-78 Typical general-purpose gear-type coupling. (*Source: Kop-Flex Inc.*)

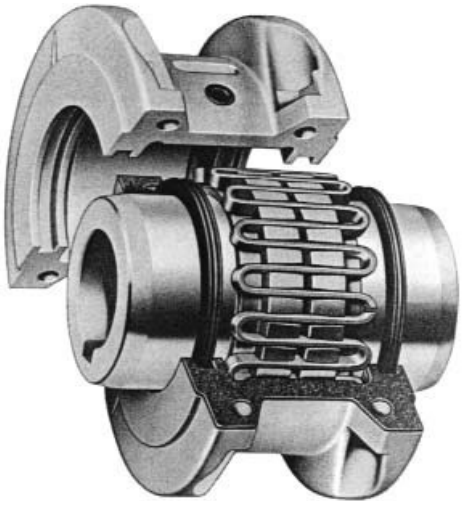


FIG. 29-79 Typical general-purpose steel-grid coupling. (*Source: The Falk Corp.*)

replacement of lubricated couplings with dry ones, particularly in machines designed for high power and high speeds. While there still are many machines equipped with lubricated couplings, new equipment is ordered with nonlubricated couplings.

POWER TRANSMISSION WITH SPEED CHANGE

Many process machines operate at speeds different from the one of their drivers. Typical of cases where the machine rotates *slower* than the driver are reciprocating compressors; typical examples of machines rotating *faster* than the drivers are centrifugal compressors driven by electric motors. In either case, *gears* are used to match the two speeds. Gears can also be designed to accommodate shafts that

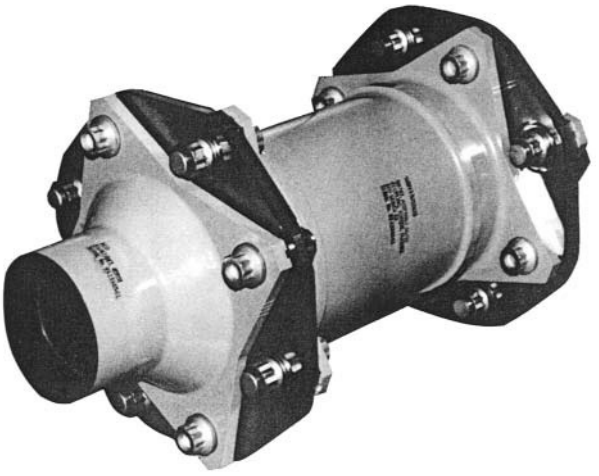


FIG. 29-80 Typical special-purpose disk-pack coupling. (*Source: Rexnord/ Thomas Coupling Div.*)



FIG. 29-81 Typical general-purpose elastomer coupling. (*Source: Rexnord Corp.*)

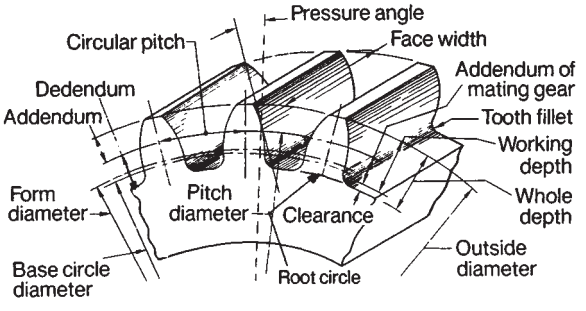


FIG. 29-82 Basic nomenclature of a gear.

are not parallel; gears can accommodate any angles between two shafts, including 90°. The following discussion is limited to gears for parallel shafts, which is the most common configuration in process machinery.

Basically, two engaging gears are two cylinders of different diameter with teeth machined on their periphery (Fig. 29-82). A gear is defined by its basic diameter (pitch diameter), its width, the number of teeth, and the angle that the teeth make in respect to the axis.

The ratio between the input-to-output shaft speeds is determined either by the ratio of the two pitch diameters or the ratio between the number of teeth:

$$i = \frac{PD_1}{PD_2}, \quad \text{or} \quad i = \frac{n_1}{n_2}, \quad \text{therefore} \quad \frac{PD_1}{PD_2} = \frac{n_1}{n_2}, \quad \text{or} \quad \frac{PD_1}{n_1} = \frac{PD_2}{n_2}$$

The ratio between the pitch diameter and the number of teeth is called the diametral pitch, and for two gears to mesh, they must have the same diametral pitch. The diametral pitch is standardized and is always an integer. For gears used in process machinery, the diametral pitch varies between 6 (coarse) and 20 (fine).

Teeth have an *involute* profile, a curve that is generated by the rolling of a straight line over a circle, as shown in Fig. 29-83. Although many curves could be used for gear teeth, the involute is the preferred one because it allows the correct engagement, even when the distance between the centers of the gears is not accurately held.

A tooth rolls over the meshing tooth only for a very small distance at the pitch diameter; above and below the pitch diameter, there is tangential sliding between the teeth, and lubrication is necessary to prevent premature wear. Because of this sliding, gears also have a certain power loss, which is about 2–3 percent per gear mesh. The heat generated by this power loss is dissipated by the lubricating oil. In high-speed gears, the oil jet is directed to where the teeth leave the engagement, as there is the point of maximum temperature.

The three most common types of cylindrical gears are shown in Fig. 29-84. *Spur* gears are the simplest, but they have the disadvantage of rough operation because as few as one or two teeth are in contact at any time. *Helical* gears have a smoother operation, but the angle of the helix generates an axial thrust on the shafts, which requires special bearings. The *double-helical* (also known as *herringbone*) gears have all the advantages of the helical gears without the axial thrust. They are also the most complicated to manufacture and are very sensitive to axial thrusts imposed from the outside on the gear shafts.

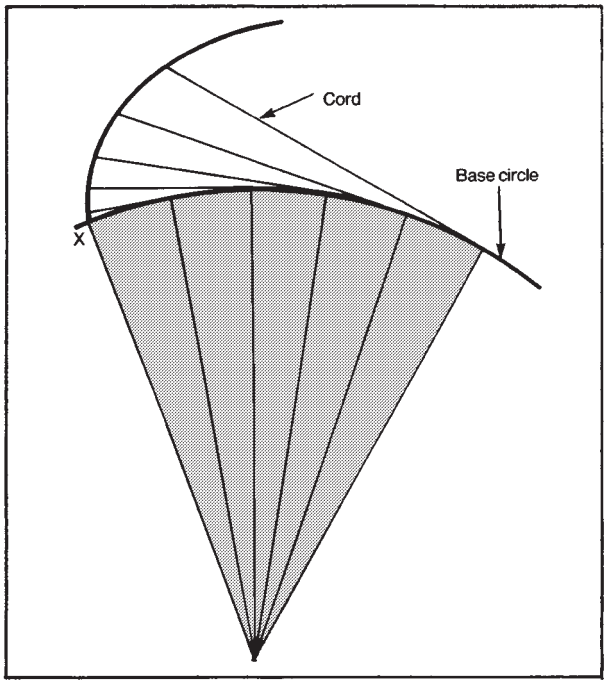


FIG. 29-83 The involute curve and its generation.

LUBRICATION OF POWER TRANSMISSION EQUIPMENT

Most machine bearings, all gears, and some couplings require lubrication. Even though a system can be designed with a direct drive, dry couplings, and magnetic bearings, such systems are still rare, and lubrication systems are ubiquitous. Lubrication systems can be as simple as a Zerk grease fitting at a motor bearing or as complicated as a console that includes a large oil tank, four or more electric-driven oil pumps, multiple filters, and oil coolers.

Grease as a Lubricant Greases are mechanical mixtures of lubricating oils and thickeners. Traditionally, metallic soaps (lithium, sodium, aluminum) were used for thickeners; although still in wide use, they are gradually being replaced with synthetic materials such as polyethylene. Greases blended with synthetic thickeners tend to be more stable but have lower resistance to high temperatures.

Greases are used as lubricants strictly because they are easily confined in a housing; greases have no additional *lubricating* properties over the oils used to blend them. Good greases are blended with special additives (just as good oils are) that can enhance their wear protection and rust protection characteristics. Greases have a paste consistency and can be very soft or very hard. The National Lubricating Grease Institute (NLGI) has established a scale for the consistency of greases that ranges from #00 (the softest) to #6. Technically, the consistency of a grease is determined by measuring the penetration of a weighted cone into the surface of a grease; a larger penetration indicates a softer grease. Unfortunately, the penetration value gives no indication about the lubricating properties of a grease; two greases can have the same consistency, but one may be blended with a high-viscosity, highly refined oil and have only 6 percent thickener, while the other may be blended with a low-viscosity, low-quality oil but have as much as 20 percent thickeners. Manufacturers may only label a grease container as "#2 lithium grease," which is not sufficient information. A complete specification sheet, however, is provided upon request. Larger manufacturers also publish a *digest*, in booklet form, that contains technical data on all their products.

There are hundreds of types of greases available, and machinery manufacturers usually provide a guideline for the greases to be used on their equipment. There are also highly specialized greases, such as the ones that can be used in food processing machinery, or the ones used in nuclear power stations.

To explain why greases cannot be used indiscriminately, the grease requirements for ball bearings and flexible couplings will be compared. Ball bearings require greases that channel, bleed, and contain a low-viscosity oil. Couplings require greases that do not channel, do not bleed, and contain a high-viscosity oil.

Channeling is required for ball bearings so that the balls can roll freely inside the bearing. Without a channel, there will be a high resistance to ball movement, and bearings would operate hot. Bleeding (slow release) of oil is required so that the balls are continuously supplied with the needed lubricant. A high-viscosity oil in a ball bearing would cause the balls to skid (hydroplane) and suffer severe scoring.

Couplings need greases that are very soft (NLGI #0 or #1) so that the spaces around the teeth are always filled with grease. Channeling would allow for metal-to-metal contact and rapid wear would occur. Because coupling rotation subjects greases to high centrifugal acceleration (that can exceed 10,000 Gs), bleeding would rapidly separate the soaps from the grease, and the oils would quickly escape, causing couplings to operate dry. Coupling teeth do not roll on each other; the

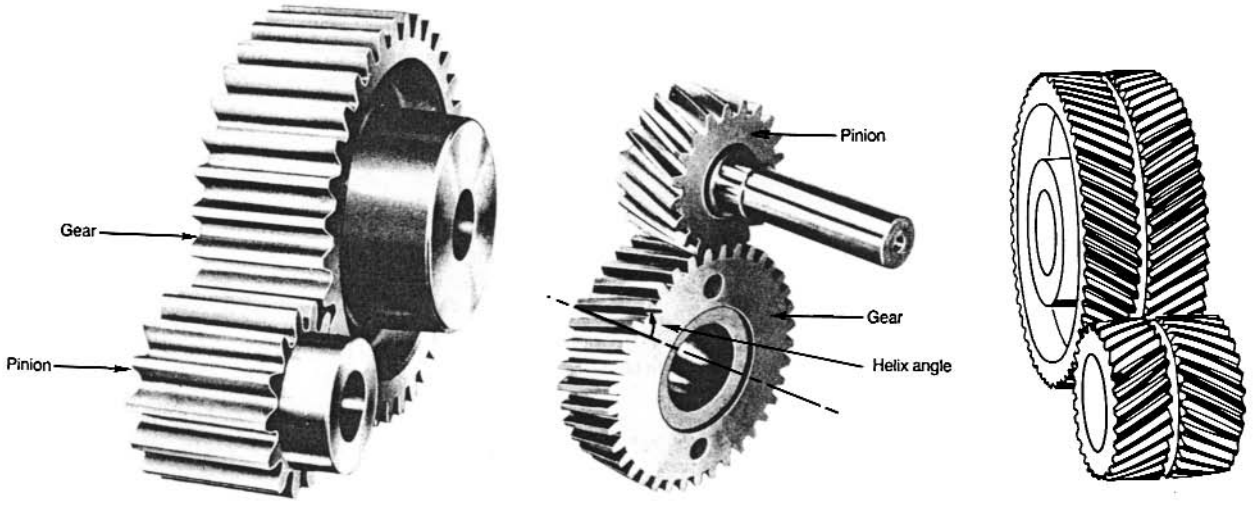


FIG. 29-84 The spur, helical, and double-helical gears.

motions in couplings are reciprocating and sliding. These motions are best lubricated by a highly viscous oil.

As was shown, using a coupling grease in a bearing could cause its failure; using a bearing grease in a coupling could cause its rapid wear.

Oil as a Lubricant Oils are used for lubrication and heat dissipation; therefore, oils are circulated through a machine (through bearings, seals, or gears), returned to a tank where dirt and water are allowed to settle out, and then pumped through coolers and filters back into the machine. Without a continuous flow of oil, machines could rapidly fail; this is why backup pumps are always provided. In systems where the main oil pump is directly driven by the machine (such as in gear boxes), two backup pumps are provided: one driven by an ac motor, which is the same size as the main one, and one driven by a dc motor (battery operated), which is small, since machines are always shut down if the main and the spare pumps fail. The dc-driven pump must only supply oil during the coast-down operation.

Filters separate and retain the dirt from the oil. They are rated based on the size of the largest particle that can pass through. Most machines in petrochemical plants use 10-micron filters. Alarms are provided to signal when a filter becomes clogged up with dirt. A valving system allows the oil to be bypassed to an alternate filter, while the element of the first one is replaced. Filter elements can be made of a wire mesh, a wire loop (closely spaced), or pleated fiber mats. The wire-loop filters are self-cleaning, as the cylindrical element slowly rotates against a wire comb; however, they cannot filter fine particles.

Oil coolers either dissipate the heat into a water stream or the air. Water coolers (Fig. 29-85) are significantly more compact, but a supply of water is required. Air coolers (Fig. 29-86) are large and require a fan that increases the air flow over the cooling fins.

A complete lubrication console schematic is shown in Fig. 29-87. Instrumentation for the console includes thermometers, pressure switches, and flow meters.

Oils used in process machinery lubrication are generally of low viscosity and are known as turbine oils or compressor oils. Such oils would have a viscosity of 78 centiStokes at 40° C (40 Saybolt Seconds

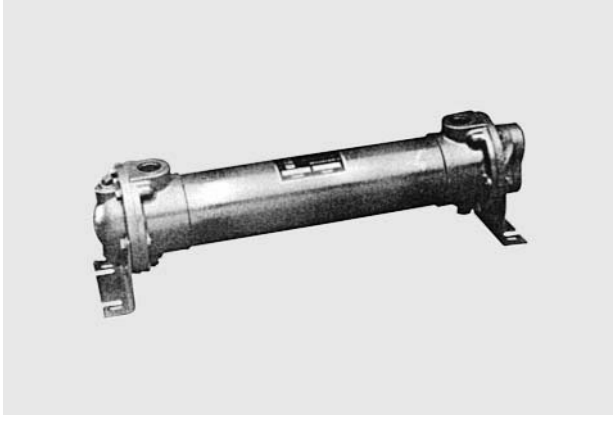


FIG. 29-85 Typical oil cooler, where the heat is transferred to water.

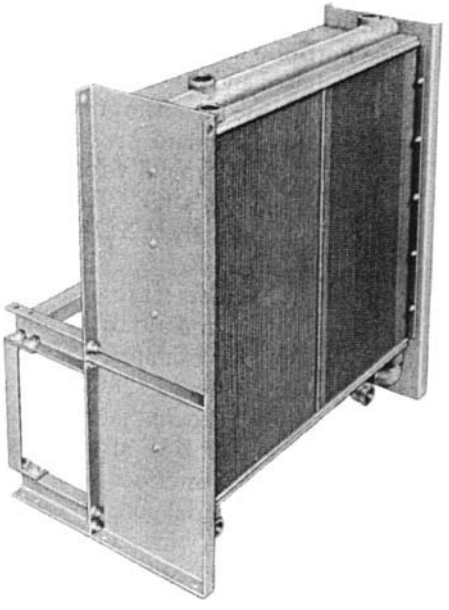


FIG. 29-86 Typical oil cooler, where the heat is transferred to air.

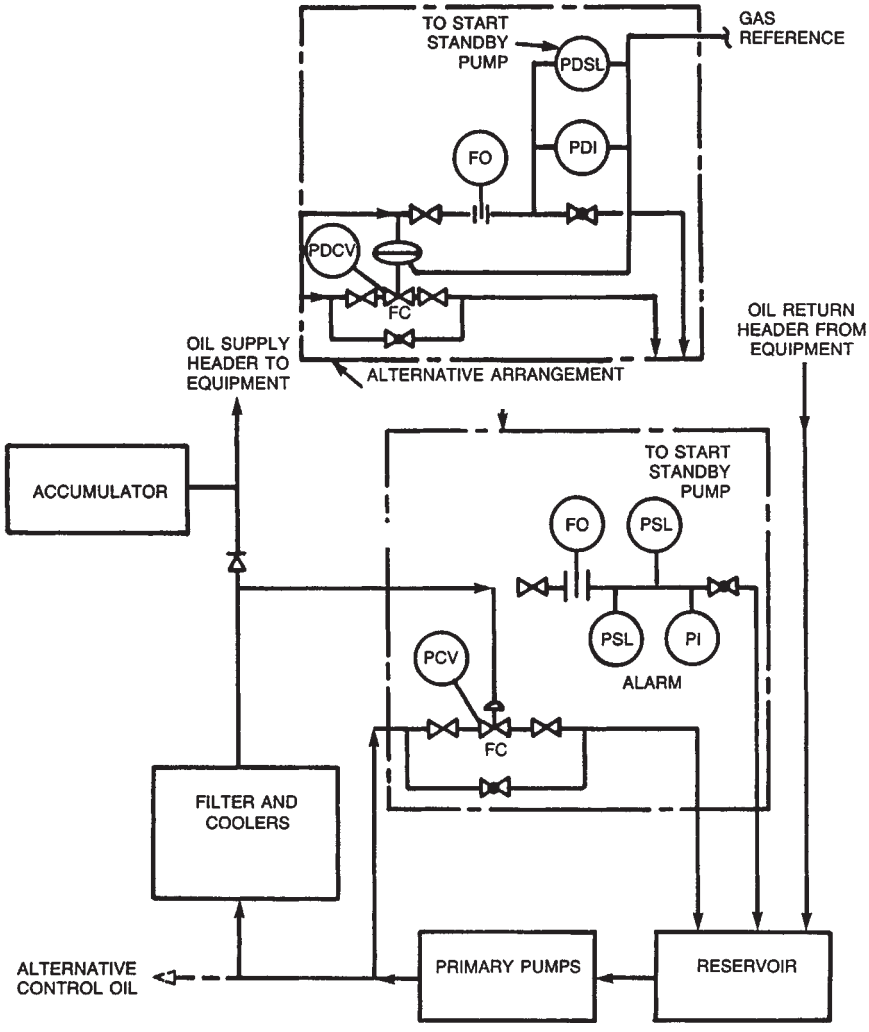


FIG. 29-87 Typical lubricating oil system for medium to large process machinery.

Universal at 100° F) and a viscosity index of 95. They contain necessary oxidation inhibitors and antiwear agents, as the same oil is used for bearings and gear lubrication. Oils tend to retain water, either from steam condensation or from condensation that occurs in the tanks. The presence of water is detrimental as it encourages the formation of acids and sludge, which can severely limit the useful life of machine components. It is customary to analyze periodically samples taken from the oil tanks and replace oils when the contamination is severe. A number of catastrophic coupling failures have been attributed to corrosion by contaminated oils.

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Section 30

Analysis of Plant Performance

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Nomenclature

Symbol	Definition	SI units	U.S. customary units
$\mathbf{B}$	Matrix of linear constraint coefficients		
$\vec{\mathbf{b}}$	Vector of bias		
b	Bias		
C_p	Heat capacity	kJ/kgmol/K	Btu/lbmole/F
c	Number of components		
$\vec{\mathbf{d}}$	Vector of weighted adjustment in measurements		
d_j	Weighted adjustment to measurement j		
$\vec{f}$	Vector of constraints		
$g\langle\rangle$	Operator on the measurements and equipment boundaries		
H_0	Null hypothesis		
H_a	Alternative hypothesis		
$\mathbf{J}$	Variance-covariance matrix of measurements		
K_{ij}	Equilibrium vaporization ratio for component i on stage j		
k	Specific rate constant		
$\mathbf{Q}$	Variance-covariance matrix of measurement adjustments		
Q	Heat transfer	kJ/hr	Btu/hr
Q_{jj}	Variance of adjustment to measurement j		
$\mathbf{R}$	Variance-covariance matrix of constraint residuals		
R_{ii}	Variance of constraint residual i		
$\vec{\mathbf{r}}$	Constraint equation residuals		
r_j	Single constraint residual		
S	Stream flow	kgmol/hr	lbmole/hr
T	Temperature	K	°F
t	Time		
$\mathbf{X_I}$	Matrix of all measurements		
$\vec{\mathbf{X}}_\mathbf{I}^\mathbf{m}$	Vector of measurements		
$\hat{\vec{\mathbf{X}}}_\mathbf{I}^\mathbf{m}$	Vector of adjusted measurements		
$\hat{\vec{\mathbf{X}}}_\mathbf{I}^\mathbf{M}$	Vector of estimated measurements from the model		
$\delta\vec{\mathbf{X}}_\mathbf{I}$	Deviation between adjusted and measured values		
$\mathbf{X_2}$	Matrix of equipment boundaries		
$\vec{\mathbf{X}}_\mathbf{2}$	Vector of component flows		
$X_{i,j}$	Component i flow in stream j		
x_{ij}	Entry in the measurement matrix; liquid mole fraction of component i on stage j		
$\hat{x}_i$	Individual adjusted measurement		
x_i	Individual measurement		
$\tilde{x}_i$	True value of individual measurement		
$\bar{x}_i$	Mean value of individual measurement		
y_{ij}	Vapor mole fraction of component i on stage j		
$y^*_{i,j}$	Equilibrium vapor mole fraction of component i on stage j		

Greek Symbols

$\vec{\beta}$	Vector representation of parameters		
σ_i	Uncertainty in individual measurement		
θ_{ij}	Tray efficiency of component i on stage j		
ρ_j	Stream density	kg/m^3	lbm/ft^3

Superscripts

M	Measurement
$\mathbf{m}$	Measured
P	Plant
$\mathbf{T}$	Transpose
T	Total

Subscripts

i	Matrix, vector position
j	Matrix, vector position

GLOSSARY

accuracy Proximity of the measurements to actual values. Data frequently contain bias, a deviation between the measurement and the actual value. The smaller the deviation, the greater the accuracy.

bias Offset between the measurement and the actual value of a measurement.

equipment boundary Limit in equipment operation. This could refer to design limits such as operating pressure and temperature. More often, the concern of the plant-performance analyst is the upper and lower operating limits for the equipment. These boundaries typically describe an operating range beyond which the equipment performance deteriorates markedly.

equipment constraints Limits beyond which the equipment cannot be operated, either due to design or operating boundaries.

fault detection Process of identifying deteriorating unit operating performance. Examples are instrument failure, increased energy consumption, and increased catalyst usage.

gross error Extreme systematic error in a measurement. The bias or systematic error is sufficiently large to distort the reconciliation and model development conclusions. Gross errors are frequently identified during rectification. Validation steps also are used to identify gross errors in measurements.

identification Procedure for developing hypotheses and determining critical measurements. Identification requires an understanding of the intent of the process and intent of the plant-performance analysis to be conducted.

interpretation Procedure for using the plant measurements or adjustments thereof to troubleshoot, detect faults, develop a plant model, or estimate parameters.

measurements Plant information. These provide a window into the operation. They may consist of routinely acquired information such as that recorded by automatic control systems or recorded on shift logs, or they may consist of nonroutine information acquired as part of a plant test.

model Qualitative or quantitative relationship between operating specifications and products. The quantitative model can be relational (e.g., a linear model) or physical (e.g., one comprised of appropriate material and energy balances, equilibrium relations, and rate relations). The parameters of these models (e.g., linear coefficients in the relational model; or tray efficiency, reactor volume efficiency, and heat transfer coefficients in a physical model) can be estimated from plant data.

plant A group of processing units. Within this context, it is the entire processing facility, typically too large to be the focus of a single plant-performance analysis. The terminology in plant-performance

analysis is inconsistent. Often the study is of a particular unit and rarely of the entire plant. However, the terms *plant test* and *plant data* refer to unit tests and unit data and will be used consistent with *practice.*

parameters Model constants that relate the operating specifications to measures of product quality and quantity. Estimation of these is a frequent goal of plant-performance analysis.

precision Measurement of the random deviations around some mean value. Precision is compromised by sampling methods, instrument calibrations, and laboratory calibrations. Reconciliation methods have been developed to minimize the impact of measurement precision.

process constraints Chemical engineering fundamental relations for the unit. Examples include material balances, energy balances, hydraulic balances and, at times, thermodynamic equilibria. These constraints may be equality constraints such as material balances or inequality constraints such as those found in hydraulic balances (i.e., $P_{out} \leq P_{in}$ for a process vessel). Obvious process constraints may not always apply due to internal or external leaks, vents, and process misunderstanding.

reconciliation Procedure for the adjustment of the measurements to close the process constraints. The purpose of reconciliation is to provide a set of measurements that better represent the actual plant operation.

rectification Procedure for the identification of measurements that contain gross errors. This process is frequently done simultaneously or cyclically with the reconciliation.

systematic error Measure of the bias in the measurements. It is a constant deviation or offset between the measurement and the actual value. This term is frequently used interchangeably with *bias.*

troubleshooting Procedure to identify and solve a problem in operating unit. This is the most frequent interpretation step in plant-performance analysis.

uncertainty A general term used for measurement error. This includes random and systematic errors in measurements.

unit Battery limits of equipment under study. The unit under study may consist of a single piece of equipment, a group (e.g., a distillation tower with auxiliary equipment), an entire process (e.g., reactors and the corresponding separation train), or the entire plant.

unit test Special operating procedure. The unit is operated at prescribed conditions. Special measurements may be made to supplement routine ones. One of the principal goals is to establish nearly constant material and energy balances to provide a firmer foundation for model development.

validation Procedure for screening measurements to determine whether they are consistent with known unit characteristics. Measurements are compared to other measurements, expected operating limits, actual equipment status, and equipment performance characteristics. It is a useful tool to eliminate potentially distorting measurements from further consideration.

INTRODUCTION TO ANALYSIS OF PLANT PERFORMANCE

MOTIVATION

The goal of plant-performance analysis is to develop an accurate understanding of plant operations. This understanding can be used to:

- Identify problems in the current operation.
- Identify deteriorating performance in instruments, energy usage, equipment, or catalysts.
- Identify better operating regions leading to improved product or operating efficiency.
- Identify a better model leading to better designs.

The results of plant-performance analysis ultimately lead to a more efficient, safe, profitable operation.

FOCUS

Section 30 is written for engineers responsible for day-to-day interpretations of plant operation, those responsible for developing unit (plant) tests, and those responsible for analyzing plant data. The content focuses on aspects of troubleshooting, fault detection, parameter estimation, and model discrimination. In order to reach reliable conclusions, methods of identification, validation, reconciliation, rectification and interpretation are included. The emphasis is on guidelines that assist in avoiding many of the pitfalls of plant-performance analysis. While there are numerous mathematical and statistical methods in the technical literature, most of them apply only to restricted plant situations atypical of normal operations or to situations where enormous amounts of measurements are handled on a routine basis. Typical plant measurements are incomplete, their statistical distributions are unknown, the plant fluctuations are too great, and/or the volume of data makes the methods intractable. The numerical methods are useful to provide some insight, and an overview is presented. However, because of the limitations to measurement and numerical methods, the engineering judgment of plant-performance analysts is critical. Analysts must develop an accurate understanding of plant operations in order to draw valid conclusions about current operation, alternative operating regimes, and proposed designs founded upon the current plant configuration.

OVERVIEW

Historical Definition Plant-performance analysis has been defined as the reconciliation, rectification, and interpretation of plant measurements to develop an adequate understanding of plant operation. Measurements taken from the operating plant are the foundation for the analysis. The measurements are reconciled to meet the constraints on the process, such as material balances, energy balances, and phase relations. The measurements are rectified to identify and eliminate those measurements that contain bias (i.e., systematic errors) sufficiently large to distort conclusions. The data are interpreted to troubleshoot, develop plant models, or estimate values for significant operating parameters. Ultimately, the results are used to discriminate among causes for deterioration of performance, operating regions, models, and possible operating decisions. The purpose of plant-performance analysis is to understand plant operations such that relational or physical models of the plant can be developed. The intended results are better profits, better control, safer operation, and better subsequent designs.

Plant-Performance Triangle This view of plant-performance analysis is depicted in Fig. 30-1 as a plant-performance triangle. Figure 30-2 provides a key to the symbols used.

The three vertices are the operating plant, the plant data, and the plant model. The plant produces a product. The data and their uncertainties provide the history of plant operation. The model along with values of the model parameters can be used for troubleshooting, fault detection, design, and/or plant control.

The vertices are connected with lines indicating information flow. Measurements from the plant flow to plant data, where raw measurements are converted to typical engineering units. The plant data information flows via reconciliation, rectification, and interpretation to the plant model. The results of the model (i.e., troubleshooting, model building, or parameter estimation) are then used to improve plant operation through remedial action, control, and design.

Unit (Plant) Data Measurements supporting plant-performance analysis come from daily operating logs, specific plant tests, automatic data acquisition, and specific measurement requirements. Examples of these data include temperatures, pressures, flows, compositions, elapsed time, and charge volume. The data are all subject to random errors from a variety of sources ranging from plant fluctuations and sampling technique through instrument calibration to laboratory methodology. The random errors define the precision in the data.

The measurements are also subject to systematic errors ranging from sensor position, sampling methods, and instrument degradation

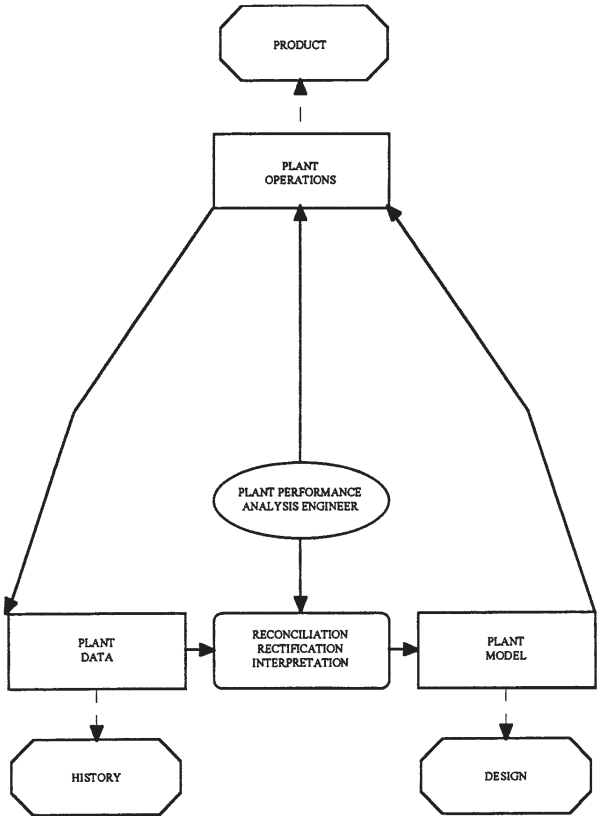


FIG. 30-1 Simplified plant performance analysis triangle.

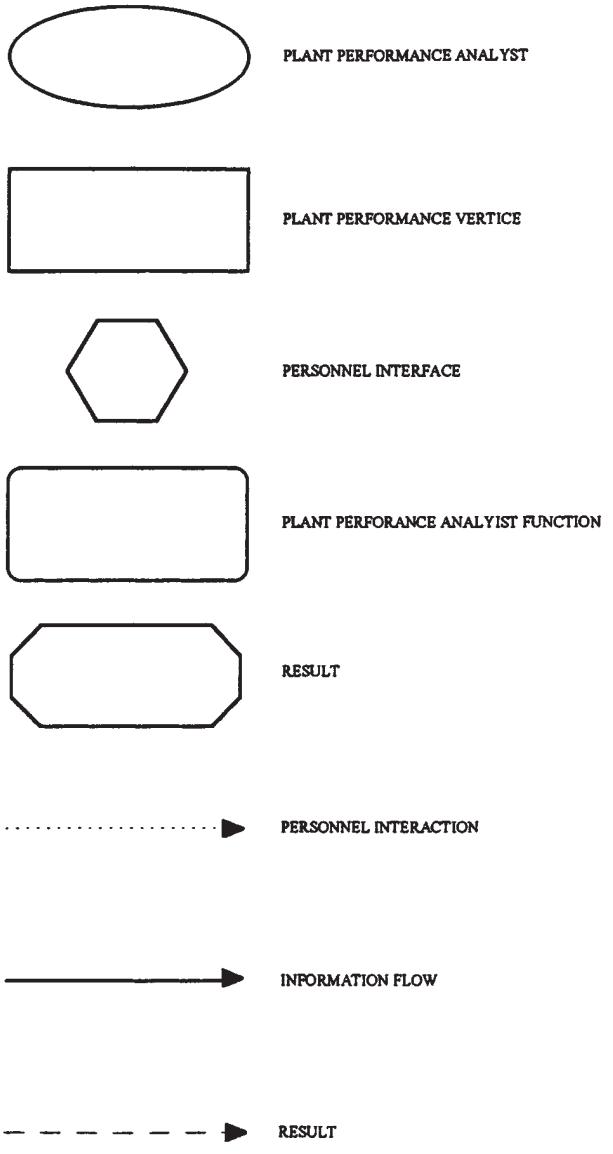


FIG. 30-2 Symbol key used in plant performance triangle.

to miscalibration in the field and laboratory. The systematic errors define the accuracy in the data.

These measurements with their inherent errors are the bases for numerous fault detection, control, and operating and design decisions. The random and systematic errors corrupt the decisions, amplifying their uncertainty and, in some cases, resulting in substantially wrong decisions.

Role of Plant-Performance Analysts In this simplified representation, the principal role of analysts is to recognize these uncertainties; to accommodate them in the analysis; and to develop more confident control, operating, or design decisions. The analysts recognize and quantify these uncertainties through repeated measurements and effective communication with equipment and laboratory technicians. They validate the data comparing them to known process and equipment information. They accommodate these errors through reconciliation—adjusting the measurements to close the process constraints. Example constraints include process constraints such as material balances, energy balances, equilibrium relations (occasionally), elapsed time, and so on; and equipment constraints or boundaries that define the limitations of equipment operation. The reconciliation literature focuses primarily on process constraints, but it is important to include equipment constraints and boundaries to ensure correct measurement adjustment.

During reconciliation, measurements in which the analysts have a high degree of confidence are adjusted little, if at all, to meet the constraints, while adjustments for less reliable measurements are greater. Correct reconciliation minimizes the impact of measurement error and results in adjusted measurements that represent plant operation better than the raw ones. Traditionally, analysts have adjusted the measurements intuitively, relying on their experience and engineering judgment. The purpose of mathematical and statistical algorithms developed over the past several years is to perform these adjustments automatically. However, algorithmic adjustment is subject to many of the same pitfalls that exist for intuitive adjustment. Both intuitive and algorithmic adjustment require correct estimates for uncertainty in the measurements. Both methods also require a correct implicit model of the plant. Without correct measurement error estimates and constraints, reconciliation will add bias to the adjusted measurements. For example, an unrecognized leak or vent invalidates the material-balance constraints developed from the implicit plant model, and either intuitive or algorithmic adjustment of data to meet invalid constraints adds systematic error to the adjusted measurements. Even when reconciliation is done algorithmically, the experience and judgment of the analysts are crucial.

The primary assumption in reconciliation is that the measurements are subject only to random errors. This is rarely the case. Misplaced sensors, poor sampling methodology, miscalibrations, and the like add systematic error to the measurements. If the systematic errors in the

measurements are large and not accounted for, all reconciled measurements will be biased. During the measurement adjustment, the systematic errors will be imposed on other measurements, resulting in systematic error throughout the adjusted measurements.

Rectification accounts for systematic measurement error. During rectification, measurements that are systematically in error are identified and discarded. Rectification can be done either cyclically or simultaneously with reconciliation, and either intuitively or algorithmically. Simple methods such as data validation and complicated methods using various statistical tests can be used to identify the presence of large systematic (gross) errors in the measurements. Coupled with successive elimination and addition, the measurements with the errors can be identified and discarded. No method is completely reliable. Plant-performance analysts must recognize that rectification is approximate, at best. Frequently, systematic errors go unnoticed, and some bias is likely in the adjusted measurements.

The result of the reconciliation/rectification process is a set of adjusted measurements that are intended to represent actual plant operation. These measurements form the basis of the troubleshooting, control, operating, and design decisions. In order for these decisions to be made, the adjusted measurements must be interpreted. Interpretation typically involves some form of parameter estimation. That is, significant parameters—tray efficiency in a descriptive distillation model or linear model parameters in a relational model—are estimated. The model of the process coupled with the parameter estimates is used to control the process, adjust operation, explore other operating regimes, identify deteriorating plant and instrument performance or to design a new process. The adjusted measurements can also be interpreted to build a model and discriminate among many possible models. The parameter estimation and model building process is based on some form of regression or optimization analysis such that the model is developed to best represent the adjusted measurements. As with reconciliation and rectification, unknown or inaccurate knowledge of the adjusted measurement uncertainties will translate into models and parameter estimates with magnified uncertainty. Further, other errors such as those incorporated into the database will corrupt the comparison between the model and adjusted measurements. Consequently, parameters that appear to be fundamental to the unit (e.g., tray efficiency) actually compensate for other uncertainties (e.g., phase equilibria uncertainty in this case).

Extended Plant-Performance Triangle The historical representation of plant-performance analysis in Fig. 30-1 misses one of the principal aspects: identification. Identification establishes troubleshooting hypotheses and measurements that will support the level of confidence required in the resultant model (i.e., which measurements will be most beneficial). Unfortunately, the relative impact of the measurements on the desired end use of the analysis is frequently overlooked. The most important technical step in the analysis procedures is to identify which measurements should be made. This is one of the roles of the plant-performance engineer. Figure 30-3 includes identification in the plant-performance triangle.

The typically recorded measurements in either daily operations or specific plant-performance tests are not optimal. The sampling locations were not selected with troubleshooting, control, operations, or model building as the focus. Even if the designers analyzed possible sample locations to determine which might maximize the information contained in measurements, it is likely that the actual operation is different from that envisioned by the designers or control engineers. More often, the sample locations are based on historic rules of thumb whose origins were likely based on convenience. Thus, for a given measurement, the amount of information leading to accurate parameter estimates is limited. Greater model accuracy can be achieved if locations are selected with the end use of the information well defined. It is necessary to define the intended end-use of the measurements and then to identify measurement positions to maximize the value in testing hypotheses and developing model parameter estimates.

END USE

The goal of plant-performance analysis is to improve understanding, efficiency, quality, and safety of operating plants. The end use must be established to focus the analysis. Figure 30-3 shows the three principal categories of end use improvements. The criteria for accuracy may vary among the categories requiring different numbers and levels of accuracy in the measurements.

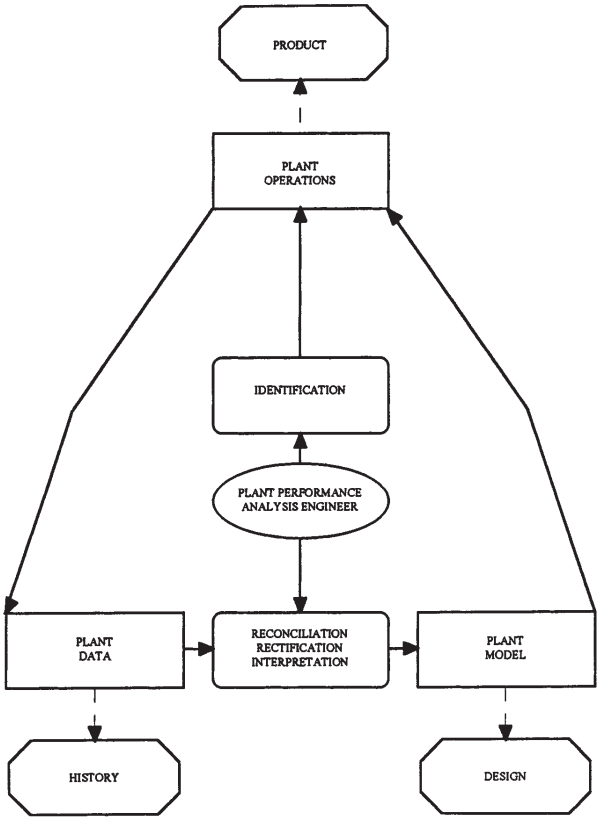


FIG. 30-3 Extended plant performance triangle.

Plant Operation The purpose is to maintain and improve performance (i.e., product quality, rate, efficiency, safety, and profits). Examples include identification of plant conditions that limit performance (troubleshooting, debottlenecking) and exploration of new operating regions.

History The history of a plant forms the basis for fault detection. Fault detection is a monitoring activity to identify deteriorating operations, such as deteriorating instrument readings, catalyst usage, and energy performance. The plant data form a database of historical performance that can be used to identify problems as they form. Monitoring of the measurements and estimated model parameters are typical fault-detection activities.

Design In this context, *design* embodies all aspects requiring a model of the plant operations. Examples can include troubleshooting, fault detection, control corrections, and design development.

TECHNICAL BARRIERS TO ACCURATE UNDERSTANDING

Limited Contained Information Data supporting the plant-performance analysis can come from daily operating logs, automatic or manual, or from formal plant tests. Daily logs consist of those measurements that the process and control designers and, subsequently, the plant engineers deem to be important in judging daily plant operation. No special operations (e.g., accumulating a constant-composition feed stock) are prerequisite for acquiring plant data of this caliber. While these data were intended to give sensitive insight into plant-performance, oftentimes they are recorded based on his-

tory and not formal analysis (i.e., their value has not been established or identified with respect to their end use). This presents the first technical hurdle—using data with limited contained information.

Formal unit (plant) tests (e.g., those developed for commissioning) usually last over a period of hours to weeks. The intent is to have the plant lined out in a representative operating regime. Feed stocks are typically accumulated in advance to ensure steady-state or controlled operation. Plant personnel are notified about the importance of the test so that they pay special attention to the operation, including charging rates, operating conditions, cycle times, and the like. Laboratory resources are dedicated beyond those normally required. A formal unit (plant) test requires significant coordination and investment. While it may give an indication of the plant capability, it is not representative of normal operation. During a unit (plant) test, greater attention and more personnel are dedicated to operation and data acquisition. Excursions in operating conditions are minimized. The data-acquisition effort should focus on sensitive measurements, providing insight beyond that gleaned from daily operations. However, oftentimes, little forethought is given to the end use of the information and the conclusions that will be drawn from it. Therefore, these additional data are not typically in the most sensitive regions of space and time. These data, too, contain less than optimal information.

There are significant technical barriers to accurate understanding from either source.

Limited Data First, plant data are limited. Unfortunately, those easiest to obtain are not necessarily the most useful. In many cases, the measurements that are absolutely required for accurate model development are unavailable. For those that are available, the sensitivity of the parameter estimate, model evaluation, and/or subsequent conclusion to a particular measurement may be very low. Design or control engineers seldom look at model development as the primary reason for placing sensors. Further, because equipment is frequently not operated in the intended region, the sensitive locations in space and time have shifted. Finally, because the cost-effectiveness of measurements can be difficult to justify, many plants are underinstrumented.

Plant Fluctuations Second, the plant is subject to constant fluctuations. These can be random around a certain operating mean; drift as feed stock, atmospheric, and other conditions change; or step change due to feed or other changes. While these fluctuations may be minimized during a formal unit (plant) test, nevertheless they are present. Given that each piece of equipment has time constants, usually unknown, these fluctuations propagate throughout the process, introducing error to assumed constraints such as material and energy balances.

Random Measurement Error Third, the measurements contain significant random errors. These errors may be due to sampling technique, instrument calibrations, and/or analysis methods. The error-probability-distribution functions are masked by fluctuations in the plant and cost of the measurements. Consequently, it is difficult to know whether, during reconciliation, 5 percent, 10 percent, or even 20 percent adjustments are acceptable to close the constraints.

Systematic Measurement Error Fourth, measurements are subject to unknown systematic errors. These result from worn instruments (e.g., eroded orifice plates, improper sampling, and other causes). While many of these might be identifiable, others require confidence in all other measurements and, occasionally, the model in order to identify and evaluate. Therefore, many systematic errors go unnoticed.

Systematic Operating Errors Fifth, systematic operating errors may be unknown at the time of measurements. While not intended as part of daily operations, leaky or open valves frequently result in bypasses, leaks, and alternative feeds that will add hidden bias. Consequently, constraints assumed to hold and used to reconcile the data, identify systematic errors, estimate parameters, and build models are in error. The constraint bias propagates to the resultant models.

Unknown Statistical Distributions Sixth, despite these problems, it is necessary that these data be used to control the plant and develop models to improve the operation. Sophisticated numerical and statistical methods have been developed to account for random errors, identify and eliminate gross errors, and develop parameter estimates. These methods require good estimates of the underlying uncertainties (e.g., probability distributions for each of the measurements). Because the probability distributions are usually unknown, their estimates are usually poor and biased. The bias is carried through to the resulting conclusions and decisions.

PERSONNEL BARRIERS TO ACCURATE UNDERSTANDING

Because the technical barriers previously outlined increase uncertainty in the data, plant-performance analysts must approach the data analysis with an unprejudiced eye. Significant technical judgment is required to evaluate each measurement and its uncertainty with respect to the intended purpose, the model development, and the conclusions. If there is any bias on the analysts' part, it is likely that this bias will be built into the subsequent model and parameter estimates. Since engineers rely upon the model to extrapolate from current operation, the bias can be amplified and lead to decisions that are inaccurate, unwarranted, and potentially dangerous.

To minimize prejudice, analysts must identify and deal effectively with personnel barriers to accurate understanding. One type of personnel barrier is the endemic mythologies that have been developed to justify decisions and explain day-to-day operation in the plant. These mythologies develop because time, technical expertise, or engineers' and operators' skills do not warrant more sophisticated or technical solutions.

Operators Operators develop mythologies in response to the pressure placed upon them for successful production quality and rates. These help them make decisions that, while not always technically supported, are generally in the correct direction. When they are not, convincing plant personnel of the deficiency in their decision structures is a difficult task.

Design and Control Engineers Equally important are the mythologies developed by the design or control engineers. Their models of plant performance are more technically sound, but may be no more accurate than the operators' mythology. Consequently, the mythology passed along by the design and control engineers can also add bias to the foundation upon which the analyst relies.

Finally, with the current developments in control technology, there is a reliance by the operating engineer on, what is in most cases, an approximate model. While the control and design engineers might fully recognize the limitations inherent in projecting beyond the narrow confines of current operation, the operating engineer will frequently believe that the control model is accurate. This leads to bias in the operation and subsequent decisions regarding performance.

Analysts The above is a formidable barrier. Analysts must use limited and uncertain measurements to operate and control the plant and understand the internal process. Multiple interpretations can result from analyzing limited, sparse, suboptimal data. Both intuitive and complex algorithmic analysis methods add bias. Expert and artificial intelligence systems may ultimately be developed to recognize and handle all of these limitations during the model development. However, the current state-of-the-art requires the intervention of skilled analysts to draw accurate conclusions about plant operation.

The critical role of analysts introduces a potential for bias that overrides all others—the analysts' evaluation of the plant information. Analysts must recognize that the operators' methods, designers' models, and control engineers' models have merit but must also beware they can be misleading. If the analysts are not familiar with the unit, the explanations are seductive, particularly since there is the motivation to avoid antagonizing the operators and other engineers.

Analysts must recognize that the end use as well as the uncertainty determines the value of measurements. While the operators may pay the most attention to one set of measurements in making their decisions, another set may be the proper focus for model development and parameter estimation. The predilection is to focus on those measurements that the operators believe in or that the designers/controllers originally believed in. While these may not be misleading, they are usually not optimal, and analysts must consciously expand their vision to include others.

In most situations, the plant was designed to be controlled and operated in a certain regime. It is likely that this has changed due to differences between the design basis and actual operation, due to operating experience and wholesale changes in purpose. Further, when developing sample, control, and measurement points, the designers/controllers may have had a model in mind for the operation. It is likely that that model is not accurate. Alternatively, they may have only used rules of thumb. Focusing only on previously selected points is limiting.

Each of the above can reduce analysts' opportunity for full understanding of the plant. Analysts must recognize that the plant operates by well-defined but not always obvious rules. It is important to identify these fundamental rules. If the analyst uses incorrect rules, the results will be further biased.

For the plant-performance analysis to be effective, the identified variables must be measured, the laboratory analysis must be correct, the simulation programs must accurately model the plant and the control recommendations must be implemented. In many settings, these aspects are not performed by plant-performance analysts. Analysts may be viewed as outsiders and operators are reluctant to modify their time-tested decision process. Laboratories geared to focusing on feed stock and product quality view unit (plant) tests as an overload. Simulation programs are not easily modified and proposed changes may not receive high priority attention. Control engineers may view modifications as an invasion of their responsibility. The plant-performance analysis milieu is much more complicated than that presented in Fig. 30-3 because of the personnel and communication barriers to implementation.

Figure 30-4 presents a more complete representation of plant-performance analysis. The information flow always faces barriers of personnel interactions. The operator must be convinced that the proposed changes and measurements will work using his/her language. The laboratory personnel must be convinced that the measurements are necessary, occasionally convinced that greater accuracy is required and that methods used are not giving results needed. Again, communication in their language must be effective. The software interaction is typically direct. However, the general nature of commercial simulators limits their effectiveness in particular situations. Occasionally, modifications are required. The software engineer is not familiar with the process and likely cannot be made aware because of proprietary considerations. This impedes communication. Finally, control engineers have been successful in establishing a control scheme which for all appearances works. Modifying the performance implies that they have not been as successful as appearances might indicate. While in all of these situations, teamwork should override these personnel considerations, it often doesn't. Consequently, communication is the paramount skill for plant-performance analysts.

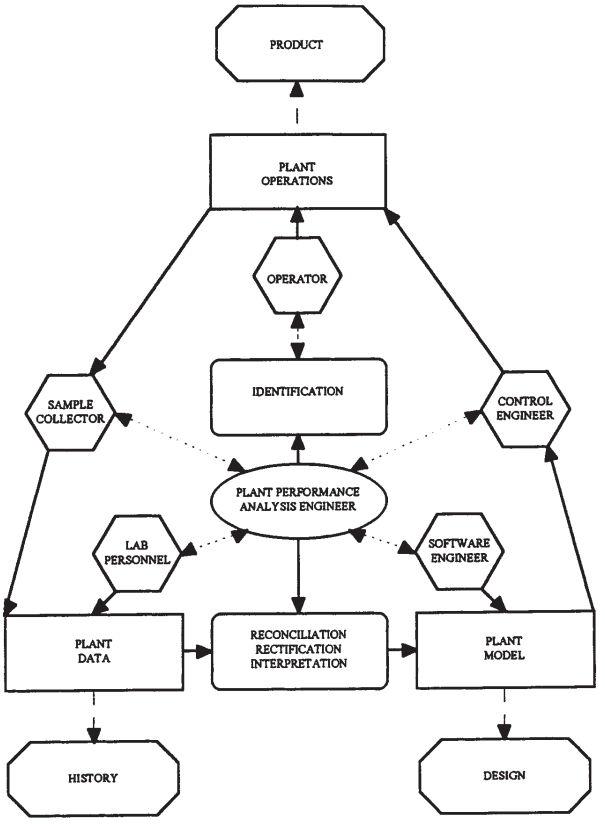


FIG. 30-4 Complete plant performance triangle including personnel interaction.

OVERALL GUIDELINES

There are four overall guidelines that analysts should keep in mind. They must recognize the difficulties associated with the limited number and accuracy of the data, overcome the plant operation mythologies, overcome the designers' and controllers' biases and, finally, override the analysts' own prejudices. The following four overall guidelines assist in overcoming the hurdles to proper plant performance.

First, any analysis must be coupled with a technically correct interpretation of the equipment performance soundly rooted in the fundamentals of mass, heat, and momentum transfer; rate processes; and thermodynamics. Pseudotechnical explanations must not be substituted for sound fundamentals. Even when the development of a relational model is the goal of the analysis, the fundamentals must be at the forefront.

Second, any analysis must recognize the nonlinearities of equipment capability. Model development must recognize that equipment fundamentals will affect conclusions and extrapolations. These boundaries and nonlinearities of equipment performance overlay the chemical engineering fundamentals and temper the conclusions.

Third, any analysis must recognize that the measurements have significant uncertainty, random and systematic. These affect any conclusions drawn and models developed. Multiple interpretations of the same set of measurements, describing them equally well, can lead to markedly different conclusions and, more significantly, extrapolations.

Fourth, communication is paramount, since successful analysis requires that those responsible for measurement, control, and operation are convinced that the conclusions drawn are technically correct and the recommended changes will enhance their performance. This is the most significant guideline in implementing the results of the analysis.

Analysis of plant performance has been practiced by countless engineers since the beginning of chemical-related processing. Nevertheless, there is no body of knowledge that has been assembled called "analysis of plant performance." The guidelines given herein are effective in plant-performance applications. There are many more practiced by others that are also effective and should be employed whenever the challenges arise. Therefore, the material discussed in this section is the initial point for analysis and should not be considered all-inclusive. The particular equipment, operations, and problems associated with any plant spawn a myriad of effective methods to approach analysis of plant performance. They should not be ignored in preference to material in this section but should be added to these to improve the accuracy of conclusions and the efficiency of approach.

PLANT-ANALYSIS PREPARATION

MOTIVATION

These are a few of the reasons to justify analysis of plant performance. Units come on-line too slowly or with extreme difficulty because heat exchangers cannot add or remove heat, venting is inadequate, or towers do not produce quality product. Units come on-line and do not meet nameplate capacity and/or quality. Unit efficiency, quality, and/or yield are below expectations because energy or catalyst usage appears too high, product compositions are below that required, or raw material usage is excessive. Unit safety is questioned because operation appears too close to equipment control limitations. Unit environmental specifications are unfulfilled. Unit operations have deteriorated from historical norms. Alternate feed stocks are available, but their advantages and disadvantages if fed to the unit are unknown. Product demand exceeds the apparent capacity of the unit requiring modifications in operating conditions, in equipment configuration, or in equipment size. Unit operation is stable, and understanding of the operation is desired.

Troubleshooting start-up, quality and capacity problems, detecting faults in deteriorating effectiveness or efficiency performance, unit modeling to examine alternate feed stocks and operating conditions, and debottlenecking to expand operations are all aspects of analysis of plant performance. Conclusions drawn from the analyses lead to piping and procedure modifications, altered operating conditions including setpoint modifications and improved designs. Analyzing plant performance and drawing accurate conclusions is one of the most difficult and challenging responsibilities of the chemical engineer (Gans, M., D. Kohan, and B. Palmer, "Systematize Troubleshooting Techniques," *Chemical Engineering Progress*, April 25–29, 1991). Measurements and data are incomplete and inaccurate. Identical symptoms come from different causes. Aspects of unit response are not readily quantified and modeled, requiring inductive, investigative reasoning. According to Gans et al. (1991), 75 percent of all plant problems are due to unidentified, inefficient plant performance ultimately traced to simple equipment problems and limitations. Another 20 percent are due to inadequate design such as those encountered in startup and quality/quantity limitations. The remainder is due to a process failure. The goal of the plant-performance analyst is to identify correctly the problems and the opportunities for changes and to quantify the potential improvements.

The opportunities leading to false conclusions and inadequate recommendations are extreme. The probability of successful completion of analysis of plant performance is greatly enhanced if the preparatory work is complete. Analysts must define the detail of study required. Analysts must understand the operation of the unit. This includes the chemical engineering fundamentals and the operator's perspective and control response. Analysts must understand historical unit performance, developing a model commensurate with the measurements available and the detail of study required. Should a unit test, short-cut or exhaustive, be required, the unit personnel must understand the goals and their responsibilities. The laboratory must be prepared to handle the overload of samples that may be necessary and be able to produce data of required quality. Personnel and the supporting supplies must be available to make measurements, gather samples, and solve problems during the course of the test.

The purpose of this section is to provide guidelines for this preparation. General aspects are covered. Preparations for the specific units can be drawn from these. Topics include analyst, model, plant, and laboratory preparation. Since no individual analyst can be responsible for all of these activities, communication with other personnel is paramount for the success of the analysis.

ANALYST PREPARATION

Analysts must have a strong foundation in plant operations and in the unit under study. The hurdles thrown at analysts increase the probability that the conclusions drawn will be incorrect. A lack of understanding in the operation of the unit increases the likelihood that the conclusions will be inaccurate. An understanding of the chemical engineering fundamentals, the equipment flowsheets, the equipment plot, the operators' understanding and interpretations, and the operators' control decisions is essential to minimize the likelihood for drawing false conclusions. Reaching this understanding prior to undertaking a unit test and the measurement interpretation will increase the success and efficiency of the analysis.

The analyst must necessarily rely on the expertise and efforts of others to operate, gather, and analyze samples and record (automatically or manually) readings. Communication of the goals, measurement requirements, and outcome to all involved is critical. It is imperative that all involved understand their responsibilities, the use of the information that they gather, and the goals of the test.

Measurement locations and methods may be different from those used daily. Analysts and the sample-gatherers must be intimately familiar with the locations, difficulties, and methods. Analysts must ensure that the methods are safe, that the locations are as indicated on the flow sheets, and that the sample-gatherers will be able to safely obtain the necessary samples.

Process Familiarization The analysts' first step in preparation for analyzing plant performance is to become completely familiar with the process. Analysts should review:

- Process flow diagrams (PFDs)
- Operating instructions and time-sequence diagrams
- Piping and instrumentation diagrams (P&IDs)
- Unit installation
- Operator perspectives, foci, and responses

The review should emphasize developing an understanding of the processing sequence, the equipment, the equipment plot, the operating conditions, instrument and sample locations, the control decisions, and the operators' perspectives. While the preparation effort may be less for those who have been responsible for the unit for a long period of time, the purpose of the test requires that the types and locations of the measurements be different from those typically recorded and typically used. The condition of these locations must be inspected. Operating specifications may be different. Therefore, refreshment is always necessary.

The intensity of the situation requiring the analysis may not allow analysts to develop a formal preparatory review of the unit as described below. Analysts must recognize that the incomplete preparation may result in a less efficient analysis of plant performance.

PFDs (process flow diagrams) display the processing sequence for the unit, the principal pieces of equipment in the unit, and the operating conditions and control scheme. The equipment sequence should represent the sequence found in the unit. The operating conditions shown on the flow sheet may be those envisioned by the designer and may not properly reflect the current conditions. These should be verified during the subsequent discussions with operators and studied through review of the shift and daily logs. Where differences are substantial, these need to be understood, as they may indicate that operating philosophy has changed significantly from that proposed by the designers. It is particularly important to verify that the control scheme represents the current control philosophy. The purpose of each piece of equipment must be understood. This understanding should include understanding of key components, temperature specifications, elapsed time constraints, and the like. The basis of the operating conditions must be understood with respect to these constraints. The PFD review is completed by developing a material balance of sufficient detail for analysts to understand the reactions and separations.

Operating instructions and time-sequence diagrams provide insight into the basis for the operating conditions. They will also provide a foundation for the subsequent discussion with operators. The time sequence diagrams may provide insight into any difficulties that will arise during the unit test.

P&IDs (piping and instrumentation diagrams) should identify instruments, sample locations, the presence of sample valves, nozzle blinding, and control points. Of particular importance are the bypasses and alternate feed locations. The isolation valves in these lines may leak and can distort the interpretation of the measurements.

Understanding the positions of sample and other measurement locations within the equipment is also important. The presence or absence of isolation valves needs to be identified. While isolation valves may be too large for effective sampling, their absence will require that pipe fitters add them such that sample valves can be connected. This must be done in advance of any test. If analysts assume that samples are from a liquid stream when they are vapor or that temperature measurements are within a bed instead of outside it, interpretation of results could be corrupted. Analysts should also develop an understanding of control transmitters and stations. The connection between these two may be difficult to identify at this level in fully computer-controlled units.

Unit layout as installed is the next step of preparation. This may take some effort if analysts have not been involved with the unit prior to the plant-performance analysis. The equipment in the plant should correspond to that shown on the PFDs and P&IDs. Where differences are found, analysts must seek explanations. While a line-by-line trace is not required, details of the equipment installation and condition must be understood. It is particularly useful to correlate the sample and measurement locations and the bypasses shown on the P&IDs to those actually piped in the unit. Gas vents and liquid (particularly water-phase) discharges may have been added to the unit based on operating experience but not shown on the P&IDs. While these flows may ultimately be small within the context of plant-performance analysis, they may have sufficient impact to alter conclusions regarding trace component flows, particularly those that have a tendency to build in a process.

Discussion with operators provide substantial insight. The purpose of the discussion should be to develop an understanding of operators' perspectives of the unit, their foci for the operation, and their decision sequence in response to deviations and off-specification products. Two additional, albeit nontechnical, goals of this discussion are to establish rapport with the operators and to learn their language. The operators will ultimately be required to implement recommendations developed by analysts. Their confidence is essential to increase the likelihood of success. The following topics should be included in the discussion.

The operators have been given instructions on unit operation. Most of these are written and should have been studied prior to the meeting. Others may be verbal or implied. While this is not optimal, verbal instructions and operating experience are still part of every unit. It is not unusual that different shifts will have different operation methods. While none of the shift operations may be incorrect, they do lead to variability in operation and different performance. "What-if" questions posed to the operators can lead to insight into operator response. This will lead to analysts gaining better understanding of the unit (Block, S.R., "Improve Quality with Statistical Process Control," *Chemical Engineering Progress*, November 1990, 38–43). The discussion with the operators must provide insight into their view of the unit operation, their focus on the operation, and their understanding of equipment limitations.

One topic of discussion is the measurements to which the operators pay the most attention (their foci). Of the myriad of measurements, there is a limited set that they find most important. These are the measurements that they use to make the short-cycle decisions. The important points to glean are the reasons they focus on these, the values and trends that they expect, and their responses to the deviations from these.

With respect to their response, the discussion should emphasize why these are important and why they adjust certain control settings. Among the deviations on which analysts should focus the discussion are the high and low alarm settings. Some alarms will require rapid response. Alarms may give insight into equipment-operation boundaries as well as process constraints.

Operators typically have long cycle measurements upon which they focus. These may be part of morning reports giving production rates, compositions, yields, and so on. They may also have some recorded measurements that they examine once per shift. Analysts should understand the importance that the operators place on these measurements and the operators' responses to them.

Analysts are typically not totally prepared to discuss the purpose of the impending test at this meeting. Therefore, this topic may be premature. There is typically a sequence of meetings between operators and analysts. The information flow in the first is typically from the operators to analysts as analysts develop their understanding and learn to communicate in the operators' language. After the analysts study the process further based on the first meeting and preliminary simulations of the unit, another meeting is useful to test the analysts' understanding and communication methods. A third meeting to discuss the impending test purpose, focus, measurements, and procedures completes this phase of the preparation.

Data Acquisition As part of the understanding, the measurements that can be taken must be understood. A useful procedure to prepare for this is to develop a tag sheet for the process (Lieberman, N.P., *Troubleshooting Refinery Processes*, PennWell Books, Tulsa, 1981, 360 pp). An example of a simplified sheet is given in Fig. 30-5.

This sheet will be used ultimately to record readings during the

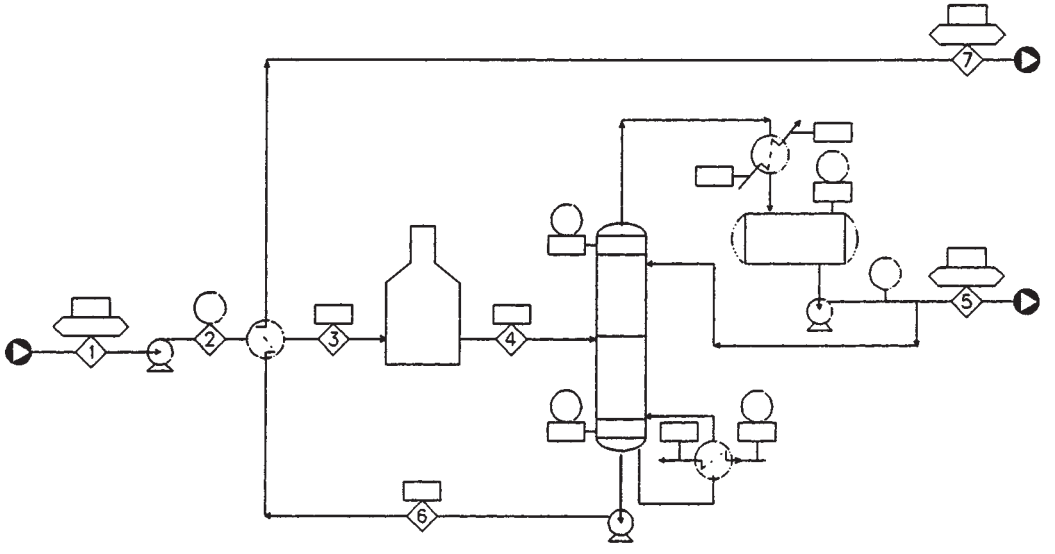


FIG. 30-5 Simplified tag-sheet for a distillation process.

plant test. It will help to develop a consistent set of measurements for the plant and help validate the measurements (identify inconsistencies). At this stage, however, it gives the analyst a visual representation of what measurements can be made. If there are sample locations, these must be added. Also, differential pressure measurements, additional flows, and utilities can be added as the unit instrumentation allows and as identified as being important during the identification step. Since identification has not been completed at this point, the measurements shown on these sheets are the ones already available on the board and in the field. The tag sheet also provides a visual point for discussion with the operators to confirm that certain measurements are made or can be made.

As part of this step, the analyst needs to develop an understanding of the uncertainty in the measurements and typical fluctuations experienced in daily operation. The uncertainties are functions of the instruments and their condition. Qualitatively, dial thermometers are less certain than thermocouples. On-line analyzers tend to be less accurate than lab analyses (assuming that the sample-gathering methodology is correct). Readings using different pressure gauges are less reliable than readings using a single pressure gauge. These random errors may be negligible in a unit that exhibits large fluctuations. The relative importance of plant fluctuations and random measurement error should be established. Multiple, rapid readings, control samples, or confirming measurements with other instruments will help establish the measurement uncertainty. Operating data will provide insight into the plant fluctuations, which can then be compared to the instrument uncertainty.

Operators frequently have insight into which instruments are accurate and which are not. If those instruments subsequently prove critical, recalibration must be done prior to the unit test. Preliminary analysis of daily measurements and practice measurements will help to identify which are suspect and require instrument recalibration prior to the unit test.

Analysts should discuss sample-collection methods with those responsible. Frequently, the methods result in biased data due to venting, failure to blow down the sample lines, and contamination. These are limitations that must either be corrected or accepted and understood. Sampling must be conducted within the safety procedures established for the unit. Since samples may be hot, toxic, or reactive in the presence of oxygen, the sample gatherers must be aware of and implement the safety procedures of the unit.

Material Balance Constraint There are two types of constraints for the unit. These are the process constraints and the equipment constraints. In each of these, there are equality constraints such as material balances and inequality constraints such as temperature limits. Analysts must understand the process and equipment constraints as part of the preparation for the unit analysis.

The most important of the process constraints is the material balance. No test or analysis can be completed with any degree of certainty without an accurate material balance. The material balance developed during this preparation stage provides the foundation for the analysts' understanding of the unit and provides an organizational tool for measurement identification. Analysts should develop a material balance for the process based on typical operating measurements. This can be compared to the design material balance. Estimates of tower splits, reactor conversions, elapsed times, and stream divisions help to identify the operating intent of the unit. Analysts must focus on trace as well as major components. The trace components will typically provide the most insight into the operation of the unit, particularly the separation trains.

During this preparation stage, analysts will frequently find that there is insufficient quantity or quality of measurements to close the material balance. Analysts should make every effort to measure all stream flows and compositions for the actual test. They should not rely upon closing material balances by back-calculating missing streams. The material balance closure will provide a check on the validity of the measurements. This preparatory material balance will help to identify additional measurements and schedule the installation of the additional instruments.

A typical material-balance table listing the principal components or boiling ranges in the process as a function of the stream location should be the result of this preliminary analysis. An example shown as a spreadsheet is given in the validation discussion (Fig. 30-18).

Energy Balance Many of the principal operating problems found in a plant result from energy-transfer problems such as fouled or blanketed exchangers, coked furnaces, and exchanger leaks. Consequently, developing a preliminary energy balance is a necessary part of developing an understanding of the unit. A useful result of the energy-balance analysis is the identification of redundant measurements that provide methods to obtain two estimates for unit performance. For example, reflux-flow and steam-flow measurements provide two routes to identifying heat input to a tower. These redundant measurements are very useful; both should be taken to provide the redundancy, and one or the other should not be ignored.

The material balance table can be supplemented with temperatures, pressures, phases, and stream enthalpies (or internal energies). Utility flows and conditions should be added to the process information.

Other Process Constraints Typical of these constraints are composition requirements, process temperature limits, desired recoveries, and yields. These are frequently the focus of operators. Violation of these constraints and an inability to set operating conditions that meet these constraints are frequently the motivation for the unit analysis.

Equipment Constraints These are the physical constraints for individual pieces of equipment within a unit. Examples of these are flooding and weeping limits in distillation towers, specific pump curves, heat exchanger areas and configurations, and reactor volume limits. Equipment constraints may be imposed when the operation of two pieces of equipment within the unit work together to maintain safety, efficiency, or quality. An example of this is the temperature constraint imposed on reactors beyond which heat removal is less than heat generation, leading to the potential of a runaway. While this temperature could be interpreted as a process constraint, it is due to the equipment limitations that the temperature is set.

Developing an understanding of these constraints provides further insight into unit operation.

Database The database consists of physical property constants and correlations, pure component and mixture, that are necessary for the proper understanding of the operation of the unit. Examples of the former are molecular weights, boiling curves, and critical properties. Example pure-property correlations are densities versus temperature, vapor pressures versus temperature, and enthalpies versus temperature and pressure. Example mixture-property correlations are phase equilibria versus composition, temperature, and pressure; kinetic rate constants versus temperature; and interfacial tension versus composition and temperature. While the material balance can be developed without most of these, the energy balance and any subsequent model cannot. Therefore, an accurate database is critical to accurate understanding of plant operation. Very often, unit model parameters will interact with database parameters. The most notable example is the distillation tower efficiency and the phase equilibria constants. If the database is inaccurate, the efficiency estimate will also be inaccurate. Therefore, whenever the goal of the unit analysis is to develop a model for operation and design, care must be taken to minimize errors in the database that can affect the accuracy of the model parameters. Inaccurate models cannot be used for sensitivity studies or extrapolation to other operating conditions.

Analysts should not rely on databases developed by others unless citations and regression results are available. Many improper conclusions have been drawn when analysts have relied upon the databases supplied with commercial simulators. While they may be accurate in the temperature, pressure, or composition range upon which they were developed, there is no guarantee that they are accurate for the unit conditions in question. Pure component and mixture correlations should be developed for the conditions experienced in the plant. The set of database parameters must be internally consistent (e.g., mixture-phase equilibria parameters based on the pure-component vapor pressures that will be used in the analysis). This ensures a consistent set of database parameters.

It is not unusual for 30–40 percent of the process design effort to be spent in developing a new database. The amount of time required at this stage in the analysis of plant performance for analysis of the unit

should be equivalent. The amount of effort devoted to database development becomes more intensive as the interaction between the model parameters and the database increases.

PLANT MODEL PREPARATION

Focus For the purposes of this discussion, a model is a mathematical representation of the unit. The purpose of the model is to tie operating specifications and unit input to the products. A model can be used for troubleshooting, fault detection, control, and design. Development and refinement of the unit model is one of the principal results of analysis of plant performance. There are two broad model classifications.

The first is the relational model. Examples are linear (i.e., models linear in the parameters and neural network models). The model output is related to the input and specifications using empirical relations bearing no physical relation to the actual chemical process. These models give trends in the output as the input and specifications change. Actual unit performance and model predictions may not be very close. Relational models are useful as interpolating tools.

The second classification is the physical model. Examples are the rigorous modules found in chemical-process simulators. In sequential modular simulators, distillation and kinetic reactors are two important examples. Compared to relational models, physical models purport to represent the actual material, energy, equilibrium, and rate processes present in the unit. They rarely, however, include any equipment constraints as part of the model. Despite their complexity, adjustable parameters bearing some relation to theory (e.g., tray efficiency) are required such that the output is properly related to the input and specifications. These models provide more accurate predictions of output based on input and specifications. However, the interactions between the model parameters and database parameters compromise the relationships between input and output. The nonlinearities of equipment performance are not included and, consequently, significant extrapolations result in large errors. Despite their greater complexity, they should be considered to be approximate as well.

Preliminary models are required to identify significant measurements and the complexity of model required and to test the analysis methods that will be used during the unit analysis. Effort must be devoted during the preparation stage to develop these preliminary models.

It must be recognized that model building is not the only outcome of analysis of plant performance. Many troubleshooting activities do not require a formal mathematical model. Even in these circumstances, analysts have developed through preliminary effort or experience a mental model of the relation between specifications, input, and output that provides a framework for their understanding of the underlying chemical engineering. These mental models generally take longer to develop but can be more accurate than mathematical models.

Intended Use The intended use of the model sets the sophistication required. Relational models are adequate for control within narrow bands of setpoints. Physical models are required for fault detection and design. Even when relational models are used, they are frequently developed by repeated simulations using physical models. Further, artificial neural-network models used in analysis of plant performance including gross error detection are in their infancy. Readers are referred to the work of Himmelblau for these developments. [For example, see Terry and Himmelblau (1993) cited in the reference list.] Process simulators are in wide use and readily available to engineers. Consequently, the emphasis of this section is to develop a preliminary physical model representing the unit.

Required Sensitivity This is difficult to establish *a priori.* It is important to recognize that no matter the sophistication, the model will not be an absolute representation of the unit. The confidence in the model is compromised by the parameter estimates that, in theory, represent a limitation in the equipment performance but actually embody a host of limitations. Three principal limitations affecting the accuracy of model parameters are:

- Interaction between database and model parameters
- Interaction between measurement error and model parameters
- Interaction between model and model parameters

Three examples are discussed.

Tray efficiency is one example of the first interaction. Figure 30-6 is a representation of a distillation tray.

Defining tray efficiency as the difference between the actual and the equilibrium vaporization, the efficiency is:

$$\theta_{i,j} = \frac{y_{i,j} - x_{i,j}}{y^*_{i,j} - x_{i,j}}$$

where

$$y^*_{i,j} = K_{i,j} x_{i,j}$$

Tray efficiency $\theta_{i,j}$ is supposed to represent a measure of the deviation from equilibrium-stage mass transfer assuming backmixed trays. However, the estimate of tray efficiency requires accurate knowledge of the equilibrium vaporization constant. Any deviations between the actual equilibrium relation and that predicted by the database will be embodied in the tray efficiency estimate. It is a tender trap to accept tray efficiency as a true measure of the mass transfer limitations when, in fact, it embodies the uncertainties in the database as well.

As another example of the first interaction, a potential parameter in the analysis of the CSTR is estimating the actual reactor volume. CSTR shown in Fig. 30-7. The steady-state material balance for this CSTR having a single reaction can be represented as:

$$0 = X_{i,1} - X_{i,2} - V_r k f(\vec{\mathbf{X}}_2, S_2, \rho_2)$$

where X_i is the flow of component i, V_r is the reactor volume, k is the rate constant at the reactor temperature, $\vec{\mathbf{X}}_2$ is the vector of component flows in stream 2, S_2 is the stream-2 flow, and ρ_2 is the stream-2 density. Any effort to estimate the reactor volume and therefore also the volume efficiency of the reactor depends upon the database estimate of the rate constant. Any errors in the rate constant will result in errors in the reactor volume estimate. Extrapolations to other operating conditions will likely be erroneous. Estimating the rate constant based on reactor volume will have the same difficulties.

The second interaction results in compromised accuracy in the parameter estimate due to the physical limitations of the process as

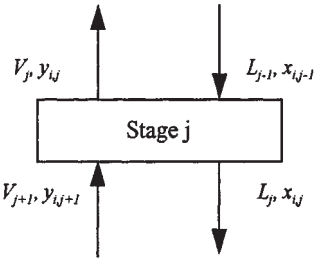


FIG. 30-6 Representation of a distillation tray numbering from the top of the column.

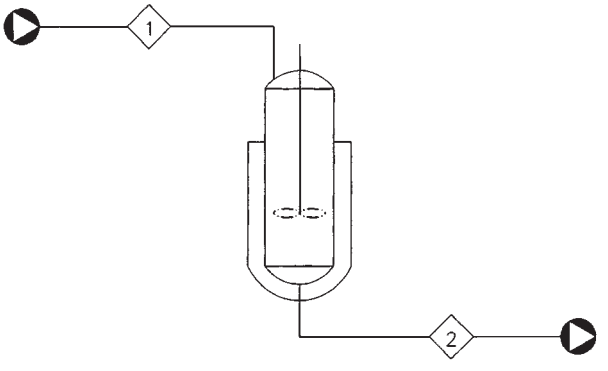


FIG. 30-7 Flow sheet of a single feed and single product CSTR.

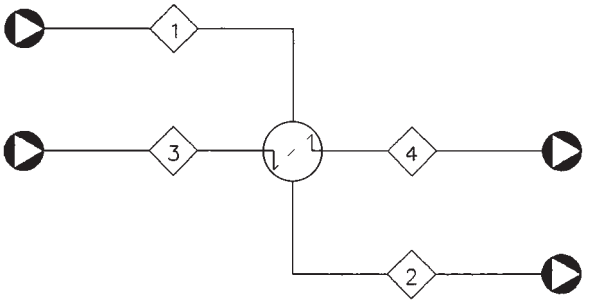


FIG. 30-8 PFD of Shell and tube heat exchanger.

embodied in the measurement uncertainties. Figure 30-8 shows a simple shell and tube heat exchanger. Many plant problems trace back to heat-transfer-equipment problems. Analysts may then be interested in estimating the heat-transfer coefficient for the heat exchanger to compare to design operation. However, this estimation is compromised when stream temperature changes are small, amplifying the effect of errors in the heat-transfer estimation. For example, the heat transfer could be calculated from the energy balance for Stream 1.

$$Q = S_1 C_p (T_2 - T_1)$$

The error in estimating the temperature difference is

$$\sigma_{\Delta T} = \sqrt{2}\sigma_T$$

The percentage error in the temperature difference translates directly to the percentage error in the estimate Q. As temperature-measurement error increases, so does the heat transfer coefficient error.

The third interaction compromising the parameter estimate is due to bias in the model. If noncondensables blanket a section of the exchanger such that no heat transfer occurs in that section, the estimated heat-transfer coefficient based on a model assuming all of the area is available will be erroneous.

The first two examples show that the interaction of the model parameters and database parameters can lead to inaccurate estimates of the model parameters. Any use of the model outside the operating conditions (temperature, pressures, compositions, etc.) upon which the estimates are based will lead to errors in the extrapolation. These model parameters are effectively no more than adjustable parameters such as those obtained in linear regression analysis. More complicated models may have more subtle interactions. Despite the parameter ties to theory, they embody not only the uncertainties in the plant data but also the uncertainties in the database.

The third example shows how the uncertainties in plant measurements compromise the model parameter estimates. Minimal temperature differences, very low conversions, and limited separations are all instances where errors in the measurements will have a greater impact on the parameter estimate.

The fourth example shows how improper model development will lead to erroneous parameter estimates. Assuming that the equipment performs in one regime and developing a model based on that assumption could lead to erroneous values of model parameters. While these values may imply model error, more often the estimates appear reasonable, giving no indication that the model does not represent the unit. More complicated examples like the kind given by Sprague and Roy (1990) emphasize the importance of the accuracy of the underlying model in parameter estimation, troubleshooting, and fault detection. In these situations, the model may describe the current operation reasonably well but will not actually describe the unit operation at other operating conditions.

Preliminary Analysis The purpose of the preliminary analyses is to develop estimates for the model parameter values and to establish the model sensitivity to the underlying database and plant and model uncertainties. This will establish whether the unit test will actually achieve the desired results.

The model parameter estimation follows the methods given in the interpretation subsection of this chapter. Analysts acquire plant measurements, adjust them to close the important constraints including the material and energy balances and then through repeated simulations, adjust parameter values to obtain a best description of the adjusted measurements. Not only does this preliminary analysis provide insight into the suitability of the model but also it tests the analysis procedures. The primary emphasis at this stage should be on developing preliminary parameter estimates with less emphasis on rigorously developing the measurement error analysis.

Once the model parameters have been estimated, analysts should perform a sensitivity analysis to establish the uniqueness of the parameters and the model. Figure 30-9 presents a procedure for performing this sensitivity analysis. If the model will ultimately be used for exploration of other operating conditions, analysts should use the results of the sensitivity analysis to establish the error in extrapolation that will result from database/model interactions, database uncertainties, plant fluctuations, and alternative models. These sensitivity analyses and subsequent extrapolations will assist analysts in determining whether the results of the unit test will lead to results suitable for the intended purpose.

PLANT PREPARATION

Intent Plant personnel, supplies, and budget are required to successfully complete a unit test. Piping modifications, sample collection, altered operating conditions, and operation during the test require advance planning and scheduling. Analysts must ensure that these are accomplished prior to the actual test. Some or all of the following may be necessary for a successful unit test.

Communication Analysts will require the cooperation of the

- Unit operators
- Unit supervisors
- Plant management
- Maintenance personnel
- Laboratory personnel

Operators are primarily concerned with stable operation and may be leery of altering the operation; they may fear that operation will drift into a region that cannot be controlled. Supervision may be reluctant despite their recognizing that a problem exists: Any deficiencies with the operation or operating decisions is their responsibility. Permission for conducting the test from the supervisor and the operators will be required. Management cooperation will be required, particularly if capital is ultimately needed. Maintenance will be called upon to make modifications to sample locations and perform a sequential pressure measurement. The laboratory personnel, discussed in detail in the next subsection, may view the unit test as an overload to available resources. These concerns must be addressed to ensure accurate sample interpretation.

Permission Analysts must have the permission of the operators and the supervisors to conduct even the most straightforward tests. While this is part of the analysts' preparation, it is important for all involved to know that analysts have that permission.

Schedule Complex tests should be done over a period of days. This provides the opportunity for the unit to be nearly steady. The advantages are that confirming measurements can be made. Scheduling a multiday test should be done when there is a likelihood that the feed stock supply and conditions will be nearly constant. The cooperation of upstream units will be required. The multiday test also requires that the downstream units can take the unit products.

The schedule should be set well in advance so that support services can provide the necessary personnel and supplies.

Simpler tests will not require this amount of time. However, they should be scheduled to minimize disruption to normal operations.

Piping Modifications One result of the inspection of the sample locations is a list of sample locations that will require modifications. The mechanical department will be required to make these modifications before the unit test is run. It is likely that the locations that are not typically used will be plugged with debris. The plugs will have to be drilled out before the test begins. Drilling out plugs presents a safety hazard, and those involved must be aware of this and follow the plant safety protocols.

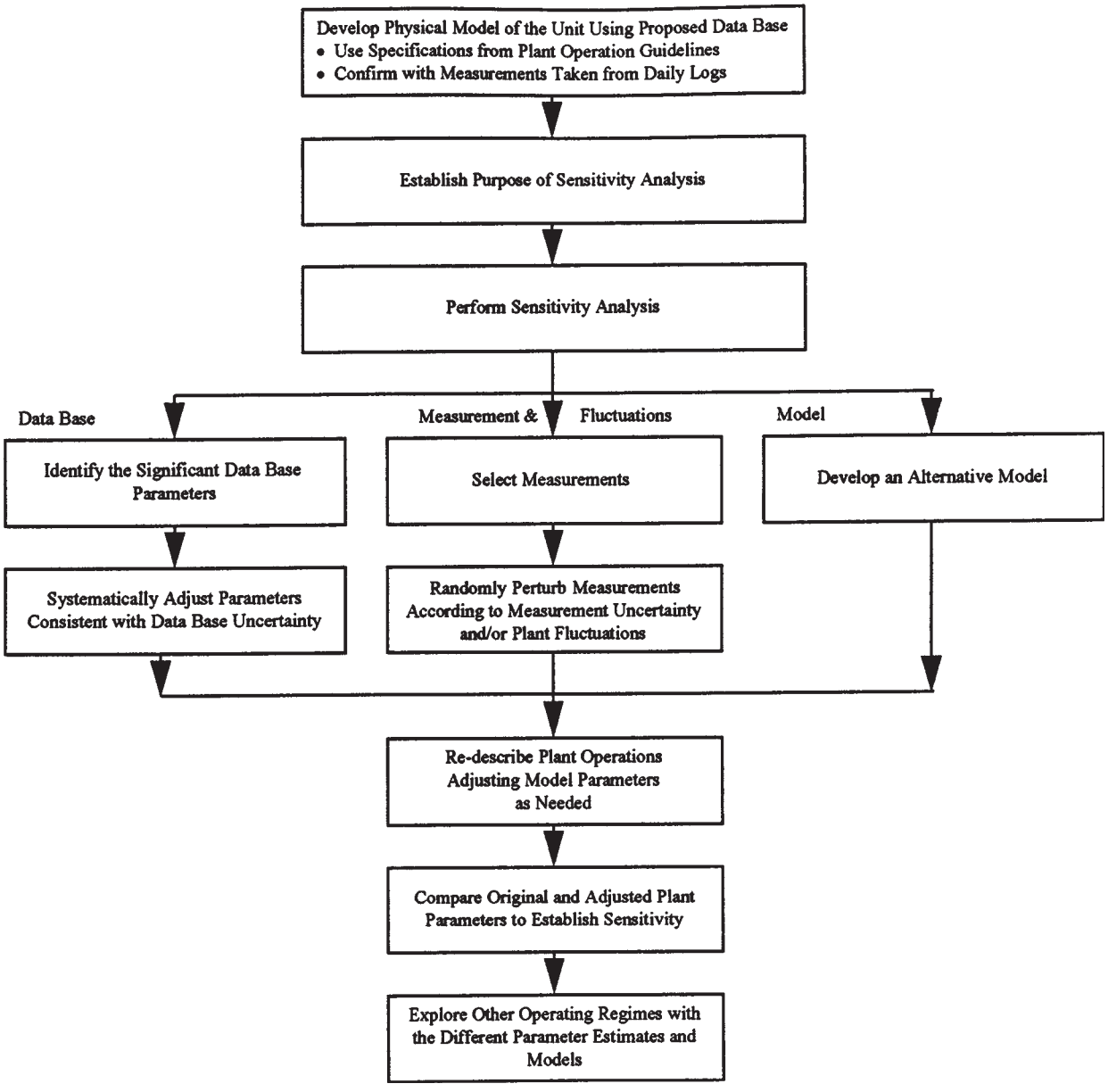


FIG. 30-9 Logic diagram for plant sensitivity analysis.

Instrumentation Calibration may be required for the instruments installed in the field. This is typically the job of an instrument mechanic. Orifice plates should be inspected for physical condition and suitability. Where necessary, they should be replaced. Pressure and flow instruments should be zeroed. A preliminary material balance developed as part of the preliminary test will assist in identifying flow meters that provide erroneous measurements and indicating missing flow-measurement points.

When doing a hydraulic test, a single pressure gauge should be used and moved from location to location. This gauge must be obtained in advance. The locations where this pressure will be measured should be tagged to assist the pipe fitter who will be responsible for moving the gauge from location to location. A walk-through with the pipe fitter responsible can be instructive for both the analysts and the fitter.

Thermocouples tend to be reliable, but dial thermometers may need to be pulled and verified for accuracy.

Sample Containers More sample containers will be required for a complex test than are typically used for normal operation. The number and type of sample containers must be gathered in advance, recognizing the number of measurements that will be required. The sample containers should be tagged for the sample location, type, and conditions.

Field Measurement Conditions Those gathering samples must be aware of the temperature, pressure, flammability, and toxic characteristics of the samples for which they will be responsible. This is particularly important when samples are taken from unfamiliar locations. Sample ports will have to be blown down to obtain representative samples. Liquid samples will have to be vented. Temperatures above

330 K (140° F) can cause burns. Pressures above atmospheric will result in flashing upon pressure reduction during venting. Venting to unplug the sample port and the sample bomb must be done properly to minimize exposure. A walk-through may be useful so that sample-gatherers are familiar with the actual location for the sample.

Operating Guidelines The test protocol should be developed in consultation with the principal operators and supervisor. Their cooperation and understanding are required for the test to be successful. Once the protocol is approved, analysts should distribute an approved one-page summary of the test protocol to the operators. This should include a concise statement of the purpose of the test, the duration of the test, the operating conditions, and the measurements to be made. The supervisor for the unit should initial the test protocol. Attached to this statement should be the tag sheet that will be used to record measurements.

Upstream and Downstream Units Upstream and downstream units should be notified of the impending test. If the unit test will last over a period of days, analysts should discuss this with the upstream unit to ensure that they are not scheduling activities that could disrupt feed to the unit under study. Analysts should seek the cooperation of the upstream units by requesting as consistent feed as possible. The downstream units should also be notified to ensure that they will be able to absorb the product from the unit under study. For both units, measurements from their instruments will be useful to confirm those for the unit under study. If this is the case, analysts must work with those operators and supervisors to ensure that the measurements are made.

Preliminary Test Operation of the unit should be set at the test protocol conditions. A preliminary set of samples should be taken to identify problems with instruments, measurements, and sample locations. This preliminary set of measurements should also be analyzed in the same manner that the full-test results will be analyzed to ensure that the measurements will lead to the desired results. Modifications to the test protocol can be made prior to exerting the effort and resources necessary for the complete test.

LABORATORY PREPARATION

Communication Laboratory services are typically dedicated to supporting the daily operation of the unit under study as well as other units in the plant. Their purpose is the routine confirmation that the unit is running properly and the determination of the quality of feed stocks. Laboratory staffing is normally set based on these routine service requirements. Consequently, whenever a plant test is conducted to address deterioration in efficiency, yield, or specifications or to develop a unit model, the additional samples required to support the test, place laboratory services in overload (Gans, M., and B. Palmer, "Take Charge of Your Plant Laboratory," *Chemical Engineering Progress,* September 1993, 26–33). If the laboratory cannot handle the analysis quickly, the likelihood of the samples reacting, leaking, or being lost markedly increases with subsequent deterioration in the accuracy of the conclusions to be drawn from the test. Therefore, adequate laboratory personnel must be accounted for early in the preparation process.

Plant-performance analysts must understand:

- Laboratory limitations
- Laboratory organization
- Laboratory measurement uncertainties
- Measurement cost
- Additional personnel requirements

The laboratory supervision and personnel must supply this information so that analysts gain this understanding.

Laboratory supervision and personnel must understand:

- Type of samples required
- Level of detail, accuracy, and precision of the samples
- Flammability, toxicity, and conditions of samples
- Anticipated schedule and duration of the test
- Justification for the overload assignments

Analysts provide this information.

The laboratory may need time to prepare for the unit test. This must be accounted for when the test is scheduled. The analysis of samples required for the unit test may focus on different composition ranges and different components than those done on a routine basis. Laboratory personnel may need to modify their methods or instruments to attain the required level of accuracy and detail. The modification, testing, and verification of the methods are essential parts of the preparation process. A practice run of gathering samples will help identify any deficiencies in the sample handling, storage, and analyses.

Without forethought, planning, and team-building, the sample analyses during the unit test may be delayed, lost, or inaccurate. The laboratory is an essential part of the unit test and must be recognized as such.

Confidence The accuracy of the conclusions drawn from any unit test depends upon the accuracy of the laboratory analyses. Plant-performance analysts must have confidence in these analyses including understanding the methodology and the limitations. This confidence is established through discussion, analyses of known mixtures, and analysis of past laboratory results. This confidence is established during the preparation stage.

Discussing the laboratory procedures with the personnel is paramount. Routine laboratory results may focus on certain components or composition ranges in the sample. The routine analyses narrow the laboratory personnel's outlook. The succinct and often misleading daily logs are the result of this focus. Analysts who have little daily interaction with the laboratory and plant may interpret daily results differently than intended. A typical example is laboratory analyses of complex streams where components are often grouped and identified as a single component. Consequently, important trace components are unanalyzed or masked. The impending plant test may require that these components be identified and quantified. The masking in the routine results can only be identified through discussion.

Even within a single sample analysis, it is likely that some of the reported concentrations are known with greater accuracy than others. Laboratory personnel will know which concentrations can be relied upon and which should be questioned. The plant-performance analyst should know at this stage which of the concentrations are of greatest importance and direct the discussion to those components.

Should the additional component compositions be required to fully understand the unit operation, the laboratory may have to develop new analysis procedures. These must be tested and practiced to establish reliability and minimize bias. Analysts must submit known samples to verify the accuracy.

Known samples should also be run to verify the accuracy and precision of the routine methods to be used during the unit test. Poor quality will manifest itself as poor precision, measurements inconsistent with plant experience or laboratory history, and disagreement among methods. Plotting of laboratory analysis trends will help to determine whether calibrations are drifting with time or changing significantly. Repeated laboratory analyses will establish the confidence that can be placed in the results.

If the random errors are higher than can be tolerated to meet the goals of the test, the errors can be compensated for with replicate measurements and a commensurate increase in the laboratory resources. Measurement bias can be identified through submission and analysis of known samples. Establishing and justifying the precision and accuracy required by the laboratory is a necessary part of establishing confidence.

Sampling Despite all of the preparation inside the laboratory, by far the greatest impact on successful measurements is the accuracy of the sampling methods. The number of sample points for a unit test are typically greater than the number required for routine sampling. It is likely that some of the sample locations, characteristics, and properties are unfamiliar to the sample-gatherers responsible for the routine ones. This unfamiliarity could lead to improper sampling, such that samples are not representative of the unit, and accidents, such that the sample gatherers are placed at risk. Part of the preparation process is to reduce this unfamiliarity to ensure safety and accuracy. The safety of the sample-gatherers is paramount and should not be compromised. Proper sampling methods accounting for volatility, flash points, toxicity, corrosivity, and reactivity should be written down for each plant and unit within the plant. The methodology must be understood and practiced.

Plant-performance analysts should be involved in reviewing the entire sampling procedure. The procedures for review are:

- Sampling locations
- Sampling safety
- Containers
- Sample transport, storage, and discharge system
- In-laboratory sampling
- Sample container cleaning

Each plant has established methods. The following should be considered during this preparation stage. Problems identified, typically during a pretest, should be solved prior to the initiation of the unit test.

Sampling locations for the unit test should be readily and safely accessible. The sample gatherer should be able to easily access the sample point. An isolation valve should be installed at the location. If a blind is installed, this should be modified in advance of the test. The sample locations shown on the P&IDs must be compared against the actual locations on the equipment. Experienced operators may provide insight into the suitability of the location in question.

The integrity and suitability of the sample containers must be established during the preparation stage. This is particularly important for those sample containers that will be used for the nonroutine measurements. Leaks jeopardize personnel and distort the resultant composition. Dirty containers contaminate samples. Open containers used for high boiling samples are unsuitable for volatile, high-temperature, pressurized samples. Trace components may preferentially adsorb onto either the container surface or the residue left in the container. Since trace components provide the greatest insight into unit operation and are the most difficult to quantify, this adsorption could lead to distorted conclusions.

Dead legs in the sample line must be discharged safely to ensure that the sample will actually be representative of the material in the unit. Without blowing down the dead leg, samples taken will be erroneous, as they may be representative of some past operating conditions. If the location is nonroutine, the sample leg may have accumulated debris. The debris could partially or totally block the line. Opening the isolation valve to blow down the line could result in a sudden, uncontrolled release, presenting a hazard to the sample gatherer.

Sample temperatures may be below ambient. If the sample vessel is liquid-full, a hazard results due to overpressurization as the liquid expands. Venting may be required, but it can distort the results. This safety hazard must be accounted for in the procedure and in interpreting the laboratory results.

Sample temperatures may be above ambient. If the temperature is significantly above ambient, personnel must be protected against burns.

Samples may separate into two or more phases as they cool in the sample line: precipitate, coagulate, and freeze. Laboratory sampling may result in nonrepresentative compositions. Heat tracing may be required and may not be installed on the nonroutine sample locations.

Validation of the measurements may require the simultaneous measurement of pressure and temperature. Typical sample locations do not have thermowells and pressure indicators. Consequently, modifications will be required to facilitate validation.

The efficient analysis will be required to minimize compromise of the analysis due to degradation (e.g., dimerization, polymerization, reactions, leaks, and contamination).

Samples will form multiple phases. The laboratory secondary sampling methods must recognize the presence of vapor, liquid, and solid phases. Improper secondary sampling methods will result in distorted measurements. These limitations must be clearly communicated to the laboratory.

Cataloging and storage of samples may inundate the laboratory, resulting in storage and retrieval problems. Mislabeled and lost samples are frequent problems. The longer the special samples remain in the laboratory, the greater the likelihood that some will be lost or mislabeled.

These potential sampling problems must be solved in advance of the unit test. The conclusions drawn from any unit test are strongly affected by the accuracy of the sampling methods and the resultant analyses. Methods should be discussed and practiced before the actual unit test. Analysts should use the trial measurements in preliminary plant-performance analysis to ensure that the results will be useful during the actual unit test.

PREPARATION GUIDELINES

Overall Everyone involved in the unit test and the analysis of measurements must understand:

- The purpose of the test
- The expectations of plant-performance analysts
- Each individual's personal responsibility to the successful outcome

Analyst Analysts must have a firm understanding of the operation of the unit. If they are not involved in the day-to-day operation or responsible for the unit, more preliminary work including process familiarization, equipment familiarization, operator interviews, and constraint limitations will be required. Even when an analyst is responsible, a review is necessary. Analysts must firmly establish the purpose of the unit test. Different levels require different budgets, personnel, and unit commitment. Additional resources beyond that required for routine measurements must be justified against the value of the measurements to the establishment of the understanding of the plant operation.

Model The level of sophistication needs to be identified. Preliminary usage of the model should identify the uniqueness of parameter estimates and conclusions to be drawn.

Plant Sufficient personnel and supplies will be required for the test. Personnel may include additional operators, sample-gatherers, pipe fitters, and engineers. Upstream and downstream units need notification so that feed and product rates can be maintained.

Laboratory The laboratory requirements and responsibilities need to be identified and accepted. The laboratory supervisor must be aware of the impending test and the likely demands placed on his/her area of responsibility. Agreement as to error levels and expected turnaround must be reached. Proper sampling methodology and storage must be established and practiced.

PLANT-PERFORMANCE ANALYSIS

THE PROBLEM

Consider Fig. 30-10. This is a single unit process with one input and two output streams. The goal for plant-performance analysis is to understand accurately the operation of this unit.

Plant-performance analysis requires the proper analysis of limited, uncertain plant measurements to develop a model of plant operations for troubleshooting, design, and control.

Measurements The potential set of data can be identified by the matrix

$$\mathbf{X}_1$$

The rows represent the type of measurement (e.g., compositions, flows, temperatures, and pressures). The columns represent streams, times, or space position in the unit. For example, compositions, total flows, temperatures, and pressures would be the rows. Streams 1, 2, and 3 would be columns of the matrix of measurements. Repeated measurements would be added as additional columns.

For more complex equipment, the columns might contain measurements for internal distillation, batch-reactor intermediate conditions, or tubular-reactor between-bed conditions. Some of these

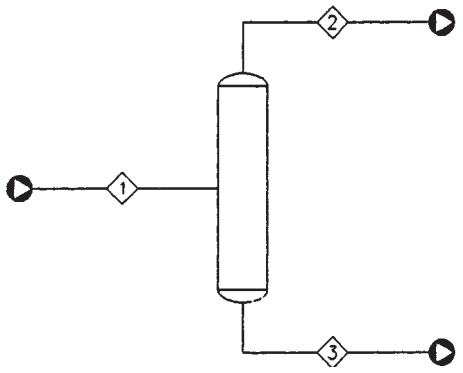


FIG. 30-10 Flow sheet of single unit process.

measurements might be recorded regularly, while others may be recorded only for the specific unit test analysis.

This matrix will necessarily be sparse. First, not all measurements can be taken for a given stream or position (e.g., a chromatographic analysis may only measure a subset of the component compositions). Second, not all streams or positions are included. Third, some of the measurements are inadequate due to bias and are discarded.

Equipment Limitations The plant-performance engineer might also have a matrix of equipment information that must be accounted for in the analysis.

$$\mathbf{X}_2$$

This matrix will contain information regarding loading characteristics such as flooding limits, exchanger areas, pump curves, reactor volumes, and the like. While this matrix may be adjusted during the course of model development, it is a boundary on any possible interpretation of the measurements. For example, distillation-column performance markedly deteriorates as flood is approached. Flooding represents a boundary. These boundaries and nonlinearities in equipment performance must be accounted for.

The purpose of the plant-performance analysis is to operate on the set of measurements obtained, subject to the equipment constraints to troubleshoot; to develop models; or to estimate values for model parameters.

$$g\langle \mathbf{X}_1^m; \mathbf{X}_2 \rangle \Rightarrow \vec{\boldsymbol{\beta}}$$

where $g\langle\rangle$ is an operator on the measurements and data. The vector $\vec{\boldsymbol{\beta}}$ is a representation of the conclusions, model, and/or equipment parameters.

Measurement Selection The identification of which measurements to make is an often overlooked aspect of plant-performance analysis. The end use of the data interpretation must be understood (i.e., the purpose for which the data, the parameters, or the resultant model will be used). For example, building a mathematical model of the process to explore other regions of operation is an end use. Another is to use the data to troubleshoot an operating problem. The level of data accuracy, the amount of data, and the sophistication of the interpretation depends upon the accuracy with which the result of the analysis needs to be known. Daily measurements to a great extent and special plant measurements to a lesser extent are rarely planned with the end use in mind. The result is typically too little data of too low accuracy or an inordinate amount with the resultant misuse in resources.

If the problem were accurately known, identification of which measurements should be taken would be exact. When the problem is initially not accurately known, the identification, measurement, and analysis procedure is iterative. Familiarity with the plant will help in identifying the measurements most likely to provide insight.

When building a model for the plant either in terms of a set of relations or in terms of a set of parameters for an existing model, it is important that the measurements contain a maximum amount of information. If the model is embodied in the symbol of the parameters, $\vec{\boldsymbol{\beta}}$, then the measurements should be made such that the measurement matrix $\mathbf{X}_1^m$ has the greatest impact on $\vec{\boldsymbol{\beta}}$. This maximizes the plant information contained in the parameters. The process is necessarily iterative. Measurements are analyzed to refine the model and optimal locations for new measurements are defined.

Analysts must recognize the above sensitivity when identifying which measurements are required. For example, a typical use of plant data is to estimate the tray efficiency or HTU of a distillation tower. Certain tray compositions are more important than others in providing an estimate of the efficiency. Unfortunately, sensor placement or sample port location are usually not optimal and, consequently, available measurements are, all too often, of less than optimal use. Uncertainty in the resultant model is not minimized.

Plant Operations Each of the elements x_{ij} in $\mathbf{X}_1^m$ have inherent error. Consequently, x_{ij} is only an estimator of the actual plant value. Or,

$$x_{ij} = \tilde{x}_{ij} + \varepsilon$$

It is useful to recognize the contributions to this error.

First, plant operations are rarely exactly as intended. While the designer may have developed all operating specifications as if the plant would operate at steady state, the plant fluctuates and drifts with time. Changes occur because of changes in feed stock, atmospheric conditions, operating conditions, controller response, and any number of factors, both known and unknown. The actual value then fluctuates around some mean operation. For example, Fig. 30-11 is a typical plant strip chart recording. The lower trace shows that the measurement is fluctuating around a mean value. The upper trace also shows fluctuation, but the mean value is changing with time.

While the random fluctuations apparent are a function of the scaling factor for the traces, the two show different amplitudes. The top trace has a relatively small fluctuation, while the bottom trace shows a larger one.

Mathematically, the mean value is the desired value for further analysis.

$$\tilde{x}_{ij} = \bar{x}_{ij} + \varepsilon_{ij}^P$$

The plant drift makes all measurements functions of time. The upper trace in the above figure shows some evidence of drift. Figure 30-12 shows a larger drift.

This drift can be represented mathematically as:

$$\tilde{x}_{ij}(t) = \bar{x}_{ij}(t) + \varepsilon_{ij}^P$$

This time dependence is different for each measurement. The fluctuation may also be a function of time.

In addition to the drift with time, step changes due to operating decisions, atmospheric changes, or other conditions result in additional time dependence. Not only is there a sudden change due to the actual decision, but also the plant changes due to the time constants. For example, Fig. 30-13 shows measurements with step changes in the operation.

Data Limitations The process of measuring $\tilde{x}_{ij}(t)$ adds additional error due to the random error of measurement. Or,

$$x_{ij}(t) = \tilde{x}_{ij}(t) + \varepsilon_{ij}^M$$
$$x_{ij}(t) = \bar{x}_{ij}(t) + \varepsilon_{ij}^P + \varepsilon_{ij}^M$$

Consequently, if these random errors are assumed to be normal, the total uncertainty including fluctuations is:

$$\sigma_{ij}^T = \sqrt{(\sigma_{ij}^P)^2 + (\sigma_{ij}^M)^2}$$

where σ replaces ε to represent a normal distribution. Therefore,

$$x_{ij}(t) = \bar{x}_{ij}(t) + \sigma_{ij}^{\mathbf{T}}$$

The problem with plant data becomes more significant when sampling, instrument, and calibration errors are accounted for. These errors result in a systematic deviation in the measurements from the actual values. Descriptively, the total error (mean square error) in the measurements is

$$\mathrm{MSE} = (\sigma_{ij}^{\mathbf{T}})^2 + (b^M)^2$$

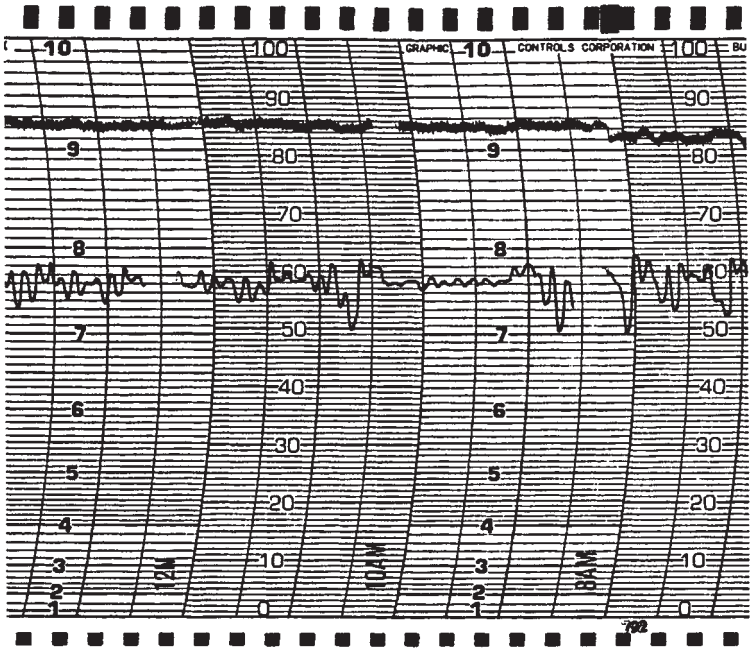


FIG. 30-11 Plant measurements showing fluctuations around a mean value.

The above assumes that the measurement statistics are known. This is rarely the case. Typically a normal distribution is assumed for the plant and the measurements. Since these distributions are used in the analysis of the data, an incorrect assumption will lead to further bias in the resultant troubleshooting, model, and parameter estimation conclusions.

Constraints Limitations Typically, the plant performance is assumed to be subject to process constraints.

$$\vec{\mathbf{f}}\langle \mathbf{X}_1 \rangle = \vec{\mathbf{0}}$$

where $\vec{\mathbf{f}}\langle\rangle$ is a vector of constraints. For the process shown in Fig. 30-10, these constraints could be, using the component flows and total flows and temperatures as the measurements:

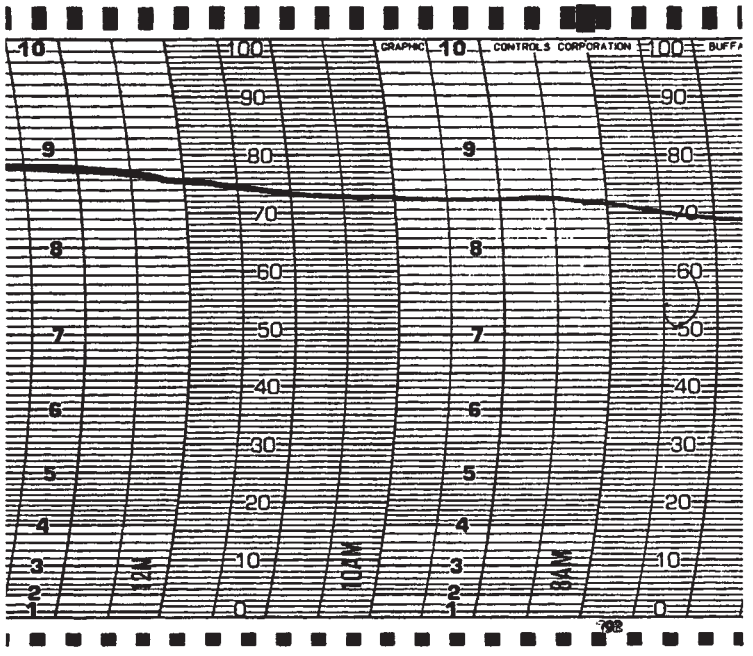


FIG. 30-12 Plant measurements showing drift with time.

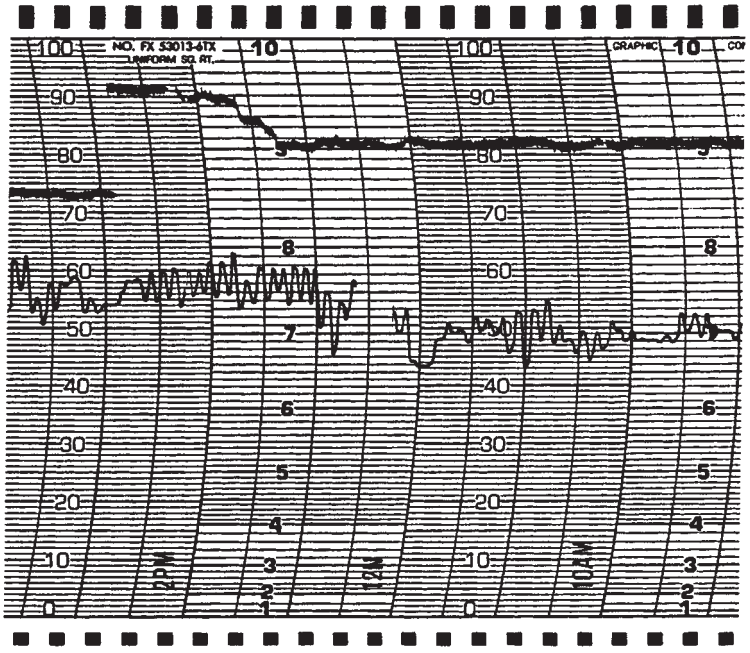


FIG. 30-13 Plant measurements exhibiting step changes, drift, and random fluctuations.

$$x_{i,1} - x_{i,2} - x_{i,3} = 0 \qquad i = 1 \ldots c$$

where c is the number of components

$$x_{c+1,1} - x_{c+1,2} - x_{c+1,3} = 0$$

$$x_{c+1,1}H_1 - x_{c+1,2}H_2 - x_{c+1,3}H_3 = 0$$

where the $c + 1$th position is the total flow. Only c of the material balance constraints are independent. Of course, the actual measurements do not close the constraints.

$$\vec{\mathbf{f}}\langle \mathbf{X}_1^m \rangle \neq \vec{\mathbf{0}}$$

To complicate matters further, because of the time dependence, leaks, or accumulation, the constraints might not actually apply such that there is a vector of unknown plant bias' associated with the constraints.

$$\vec{\mathbf{f}}\langle \mathbf{X}_1^m \rangle = \vec{\mathbf{b}}^p$$

Assuming $\vec{\mathbf{b}}^p = 0$ will potentially add bias to the interpretation of plant measurements. Further, the plant bias may to some extent mask the error in the measurements. While the designer may have envisioned a constant set of conditions or a specified time dependence, it is likely that the actual operation changes due to external factors.

The technical problem becomes one of:

$$g\langle \mathbf{X}_1^m; \mathbf{X}_2 \rangle \overset{b^o}{\Rightarrow} \vec{\boldsymbol{\beta}}$$

subject to

$$\vec{\mathbf{f}}\langle \mathbf{X}_1^m \rangle = \vec{\mathbf{b}}^p$$

This is a formidable analysis problem. The number and impact of uncertainties makes normal plant-performance analysis difficult. Despite their limitations, however, the measurements must be used to understand the internal process. The measurements have limited quality, and they are sparse, suboptimal, and biased. The statistical distributions are unknown. Treatment methods may add bias to the conclusions. The result is the potential for many interpretations to describe the measurements equally well.

Personnel Bias Because of the possibility of several interpretations of the plant-performance problem, the judgment of analysts plays a critical role. Any bias in the analysts' judgments will carry through the data analyses. To minimize this, analysts must develop an implicit model based on the fundamental rules of the plant and not on the prejudices of the operators, designer engineers, control engineers, or the analyst's own perceptions.

The following presents guidelines for identifying, validating, reconciling, rectifying, and interpreting plant measurements to remove some of the bias from the conclusions.

IDENTIFICATION

Motivation Unit tests require a substantial investment in time and resources to complete successfully. This is the case whether the test is a straightforward analysis of pump performance or a complex analysis of an integrated reactor and separation train. The uncertainties in the measurements, the likelihood that different underlying problems lead to the same symptoms, and the multiple interpretations of unit performance are barriers against accurate understanding of the unit operation. The goal of any unit test should be to maximize the success (i.e., to describe accurately unit performance) while minimizing the resources necessary to arrive at the description and the subsequent recommendations. The number of measurements and the number of trials should be selected so that they are minimized.

Often, analysts will want to run special short-term tests with the operating unit in order to identify the cause of the trouble being experienced by the unit. Operators are naturally leery of running tests outside their normal operating experience because their primary focus is the stable control of the unit, and tests outside their experience may result in loss of control. Multiple tests with few results may decrease their cooperation.

Modern petro/chemical processes provide the opportunity for gathering a large number of measurements automatically and frequently. Most are redundant and provide little additional insight into unit performance. The difficulties in handling a large amount of information with little intimate knowledge of the operation increases the likelihood that some of the conclusions drawn will be erroneous.

Therefore, the identification of appropriate tests and measurements most important to understanding the unit operation is a critical step in the successful analysis of plant performance.

Limitations Identifying the appropriate test to troubleshoot a unit problem requires hypothesis development and testing. Hypothe-

ses are based on the observed problem in current operation and the historical performance. It is the skill of analysts to develop the minimum number of hypotheses and unit tests to identify what is typically a well-hidden problem.

Identifying the minimum number of specific measurements containing the most information such that the model parameters are uniquely estimated requires that the model and parameter estimates be known in advance. Repeated unit tests and model building exercises will ultimately lead to the appropriate measurements. However, for the first unit test in absence of a model, the identification of the minimum number of measurements is not possible.

The methodology of identifying the optimum test and number of measurements has received little attention in analysis of plant performance and design literature.

Measurement Error Uncertainty in the interpretation of unit performance results from statistical errors in the measurements, low levels of process understanding, and differences in unit and modeled performance (Frey, H.C., and E. Rubin, "Evaluate Uncertainties in Advanced Process Technologies," *Chemical Engineering Progress,* May 1992, 63–70). It is difficult to determine which measurements will provide the most insight into unit performance. A necessary first step is the understanding of the measurement errors likely to be encountered.

An example adapted from Verneuil, et al. (Verneuil, V.S., P. Yan, and F. Madron, "Banish Bad Plant Data," *Chemical Engineering Progress,* October 1992, 45–51) shows the impact of flow measurement error on misinterpretation of the unit operation. The success in interpreting and ultimately improving unit performance depends upon the uncertainty in the measurements. In Fig. 30-14, the material balance constraint would indicate that $S_3 = -7$, which is unrealistic. However, accounting for the uncertainties in both S_1 and S_2 shows that the value for S_3 is -7 ± 28. Without considering uncertainties in the measurements, analysts might conclude that the flows or model contain bias (systematic) error.

Analysts should review the technical basis for uncertainties in the measurements. They should develop judgments for the uncertainties based on the plant experience and statistical interpretation of plant measurements. The most difficult aspect of establishing the measurement errors is establishing that the measurements are representative of what they purport to be. Internal reactor CSTR conditions are rarely the same as the effluent flow. Thermocouples in catalyst beds may be representative of near-wall instead of bulk conditions. Heat leakage around thermowells results in lower than actual temperature measurements.

These measurement uncertainties must be accounted for in developing hypotheses used to explain unit performance and in identifying measurements which will provide the best model of the unit.

Hypothesis Development Successful, efficient development of hypotheses and operating conditions to test them require design, operation, control, and troubleshooting experience. Understanding the relation of the fundamentals of chemical engineering, the specifications and their intent for operation, the response of equipment to upsets, and the identification of the unusual are all essential tools for developing and testing hypotheses during troubleshooting exercises. Hypothesis development is typically iterative with unit operating conditions adjusted to test a hypothesis. The results lead to other hypotheses and other operating conditions. This is an essential part of troubleshooting and model development.

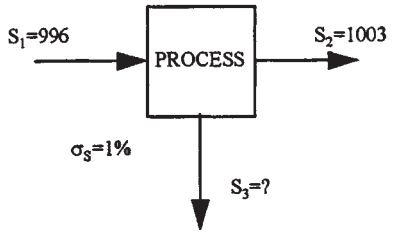


FIG. 30-14 Material balance measurements with error.

Troubleshooting is usually based on checklists developed by analysts specific to the unit and types of equipment in the unit. These checklists assist in hypothesizing the cause of observed problems based on past experience and in developing tests or measurements to confirm the hypotheses. Few published checklists exist in the literature. Most analysts develop their own based on experience. As engineers move from assignment to assignment with little direct, continued experience in the design, operation, control, and troubleshooting, the checklists are lost. The skill resides with the engineer and not with the unit. Consequently, individual checklists are developed repeatedly with little continuity unless current analysts seek out those who were once responsible for the unit. One notable exception is the set of checklists for refinery operations published by Lieberman (1981). Many of his experiences arise in and apply to other chemical engineering applications. His lists give the observed problem and possible explanations. Harrison and France (Harrison, M.E. and J.J. France, "Auxiliary Equipment: Troubleshooting Distillation Columns," *Chemical Engineering,* June 1989, 130–137) list a series of problems with corresponding causes. Symptoms in one piece of equipment may appear as a problem in another; therefore, checklists should include the potential that other equipment in the unit is the cause of the observed problem.

A proposed checklist form is given in Table 30-1. The descriptive example concerns a problem observed with distillation performance in a specific unit. It is included for descriptive purposes only and does not provide an exhaustive list of possible explanations for the observed problem. The important aspects are a clear statement of the problem; recognized changes in unit operation at the time of the observation and hypothesized causes under the categories of erroneous instrument readings; changes upstream and downstream from the unit and within the unit itself. Typical explanations under each cause category could be substantially longer than ones included in the table.

History is important is establishing hypotheses. When a problem arises in a unit, something has changed. The first step in developing a hypothesis explaining the cause of the problem is to establish that the operation has clearly changed from some earlier operation. Easily identified alterations in operation such as those that result from changes in operating specifications, equipment installations, or operator responses should be listed.

The observations may be erroneous due to misleading measurements. The basis of the observations should be examined. Instruments may have degraded. Sample lines may have become plugged. Trip settings may have changed. Where possible, these causes should be eliminated before moving to more complex explanations and tests. Many unit problems are caused by upstream or downstream units. This interaction should be identified before performing extensive tests with the unit. In the table, a sudden increase in light ends could flood the upper section of the tower. Pump cavitation may be the result of fluctuating discharge pressures in the downstream units. Corrosion in the unit may be caused by carryover from an upstream unit. Insufficient pump capacity could be caused by a changed fluid density from changed feed stock.

With the problem being identified as real and other units being eliminated as the cause, the focus can move to identifying whether the problem is with capacity or efficiency within the unit.

The following are guidelines for establishing checklists used to identify the cause of observed problems.

TABLE 30-1 Example Checklist Form

Observed problem	Increased pressure drop in the distillation column
Unit changes	Steam header pressure increase, no equipment changes
Instrument cause	DP meter reading is misleading due to failed instrument, plugged ports, etc.
Upstream cause	Increased percentage of light components fed to column resulting in flooding in rectifying section
Downstream cause	Not applicable
Capacity cause	Steam reboiler flow set above column jet flood limit
Efficiency cause	Trays plugged with polymer buildup

• Establish the timeline of the problem hypothesizing that changes in operation, equipment, or response are the root cause of the problem.
• Establish the observed problem is real by hypothesizing potential problems with instruments and instrument installations.
• Establish that the observed problem could not be caused by upstream or downstream unit performance.
• Establish that the problem is one with capacity of the unit by hypothesizing causes for the decreased unit production.
• Establish that the problem is one with efficiency of the unit by hypothesizing causes to explain the decreased performance of the unit.

Any set of guidelines must be tempered by the analysts' experience. This is an investigative process. The explanations are rarely simple. However, many exhaustive tests have been run to identify that a bypass valve or alternative feed valve had been mistakenly left open. Plant resources were misused because the simple was overlooked.

Since hypothesis development and testing frequently require alternative operating conditions, safety considerations must be paramount. The operators' concerns about loss of control are justified. When tests are planned, it must be recognized that adjustments should be slow and stepwise with time allowed for the unit to line out. All possible outcomes of the adjustments should be thought through to minimize the potential for moving the unit into an unstable operating regime.

Model Development Preliminary modeling of the unit should be done during the familiarization stage. Interactions between database uncertainties and parameter estimates and between measurement errors and parameter estimates could lead to erroneous parameter estimates. Attempting to develop parameter estimates when the model is systematically in error will lead to systematic error in the parameter estimates. Systematic errors in models arise from not properly accounting for the fundamentals and for the equipment boundaries. Consequently, the resultant model does not properly represent the unit and is unusable for design, control, and optimization. Cropley (1987) describes the erroneous parameter estimates obtained from a reactor study when the fundamental mechanism was not properly described within the model.

Verneuil et al. (Verneuil, V.S., P. Yan, and F. Madron, "Banish Bad Plant Data," *Chemical Engineering Progress*, October 1992, 45–51) emphasize the importance of proper model development. Systematic errors result not only from the measurements but also from the model used to analyze the measurements. Advanced methods of measurement processing will not substitute for accurate measurements. If highly nonlinear models (e.g., Cropley's kinetic model or typical distillation models) are used to analyze unit measurements and estimate parameters, the likelihood for arriving at erroneous models increases. Consequently, resultant models should be treated as approximations.

Recognition of measurement error, model nonlinearities, interactions, and potential fundamental oversights are an important part of the identification stage of analysis of plant performance. Repeated simulations using different models extrapolated to other operating conditions will provide insight into model viability. Model accuracy can be verified by operating the unit at different operating conditions and making appropriate measurements. Identification of these conditions and measurements is one aspect of the identification step. These model building studies to identify possible alternative models and operating conditions are useful in minimizing the impact of erroneous model development and subsequent parameter estimation.

Measurement Selection Along with the hypothesis development, the principal result of the identification step is determining which measurements will provide insight into the unit operation. This often-overlooked aspect of analysis of plant performance deserves greater attention in the plant operations and research literature. The potential resource savings resulting from minimizing the number of measurements, repeated unit tests, and associated personnel are enormous. Coupled with the benefit of developing a more robust model of the unit, this overlooked aspect of analysis of plant performance potentially outweighs the benefits of all other aspects.

The goal of measurement selection is to identify a set of measurements that, when interpreted, will lead to unique values for the model parameters, insensitive to uncertainties in the measurements. This is an iterative process where:

• A group of measurements are proposed based on preliminary model predictions
• Values for parameters are estimated using the interpretation procedures
• Simulated unit performance sensitivity to the parameter estimates is evaluated
• Alternative measurements are proposed
• The process is repeated

The optimum measurements are those taken in the unit test. Figure 30-15 provides one procedure for identifying which measurements should be taken within the plant.

A preliminary model is developed during the preparation stage. Preliminary values of the model parameters are estimated based on adjusted plant measurements. Simulations of the unit are then run to develop values for the temperatures, pressures, flows, compositions, and the like, that are representative of the unit operation. A group of measurements that could possibly be taken in the unit test is then selected. At that point, analysts have two options. In option A, the parameter estimates are perturbed, the unit resimulated, and the group of measurements compared to the set corresponding to the perturbed parameters. If the comparison is such that the simulated measurements are different beyond the experimental error, then the parameter values are unique and the group of measurements are appropriate. If they are not, the proposed measurements should be changed and the process repeated. In option B, the process is similar. The group of measurements are perturbed according to the measurement error, the parameters re-estimated, and the parameter values compared. If there is relatively little change in the parameter values, the selected measurements are acceptable. If there is a large change, the measurements do not provide a unique set of parameter estimates. Consequently, the model would be unsuitable. The measurement set needs to be modified. Once the set of measurements have been selected, the model should be examined and modified if necessary. There are two primary indications that the model may be inadequate. First, the preliminary model with the estimated parameters provide descriptions of one or more measurements representing unit behavior, particularly internal to individual pieces of equipment. Second, the values of the parameters are unrealistic.

With respect to selecting measurements, emphasis should include measurements within the equipment such as tower internal temperatures and compositions, internal reactor conditions, and intermediate exchanger temperatures in multipass exchangers. Trace component compositions provide particular insight into distillation-column performance. Those components that fall between the heavy and light keys and distribute in the products can usually be described by a variety of models and parameter estimates: They provide little insight into the column performance.

The procedure given in Fig. 30-15 leaves much to analysts. Criteria for selecting the number and location of measurements for a particular piece of equipment or unit have not been established in the literature. Therefore, there is heavy reliance on examining alternative models at the bottom of the procedure. The creativity of analysts to develop alternative explanations for performance or hypotheses explaining why the present model might be wrong is a particularly important skill.

VALIDATION

Initial Measurement Examination The process of reconciling data to constraints; rectifying data to detect and identify systematic errors; and interpreting data to troubleshoot, model-build, and estimate parameters is a time-consuming, often unnecessary, and, many times, inaccurate series of steps. Even under the most controlled circumstances, the methods often provide estimates of plant operation that are no better than that provided by the actual plant measurements. If the adjusted measurements contain significant error, the resultant conclusions could be significantly in error and misleading. Prescreening can identify measurements containing significant error and can provide insight into the plant operation.

Validation is the procedure of comparing measurements to known relations between the measurements and equipment settings (May,

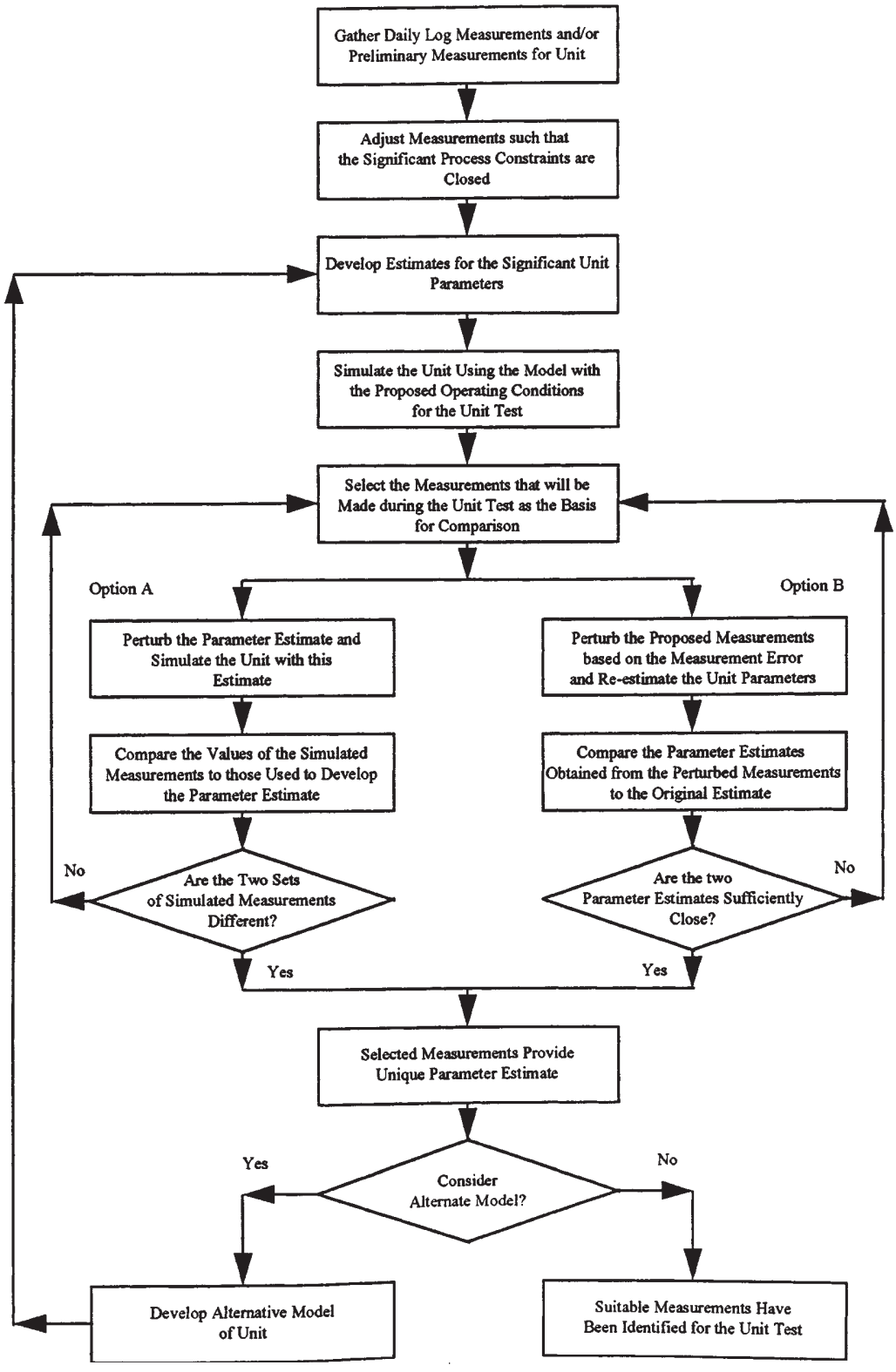


FIG. 30-15 Procedure for identifying measurements.

D.L. and J.T. Payne, "Validate Process Data Automatically," *Chemical Engineering,* June 1992, 112–116). If a measurement is clearly inconsistent with equipment operation that is known to be true, the measurement must then be deemed suspect. Validation is the procedure of comparing a measurement to one or more of the following.

- Another measurement
- An expected range
- Equipment status
- Equipment relations

If the comparison shows that the measurement is inconsistent with the comparison information, the measurement is considered suspect. If a measurement can be compared to more than one set of information and found to be inconsistent with all, it is likely that the measurement is in error. The measurement should then be excluded from the measurement set. In this section, validation is extended to include comparison of the measurements to the constraints and initial adjustment in the measurements. Validation functions as an initial screening procedure before the more complicated procedures begin. Oftentimes, validation is the only measurement treatment required prior to interpretation.

It is important to note that validation typically only brings a measurement under suspicion. It does not verify that the measurement is incorrect. Safety is paramount. Some validation analysis could result in concluding that the measurement is invalid when, in fact, the comparison information is invalid. It is not difficult to extrapolate that actions could result from this erroneous conclusion which would place maintenance and operating personnel in jeopardy. Validation merely raises suspicion; it does not confirm errors of measurement.

The greater the number of validation comparisons between the measurement and the list above, the greater the likelihood that the measurement can be identified as valid or invalid.

Measurement versus Measurement In this type of validation, a process measurement is compared against another. For example, if a separate high-level alarm indicates that a tank is overflowing but the level gauge indicates that it is in the expected range, one of these measurements is wrong. As another example, if a light component suddenly appears in the bottoms of a distillation tower and no other light components contained in the feed appear in the bottoms, the first measurement is suspect.

Measurement versus Expected Range If a steam flow is expected to vary in a relatively narrow range and the flow measurement indicates that it is twice the high value, the flow measurement is then suspect and should be reviewed. A frequent occurrence is when a measurement remains unchanged for a period of time when normal plant fluctuations should result in oscillations around a setpoint. The constant measurement would indicate that this reading is suspect.

Measurement versus Equipment State A pump off-line should have no flow. If the pump is off and the flow meter indicates that there is flow, the flow measurement is suspect.

Measurement versus Equipment Performance Pumps that are in reasonable condition typically operate within 5 percent of their pump curve. Consequently, pressures and flows that are inconsistent with the pump curve imply that the indicated flow and/or pressure are incorrect. Figure 30-16 shows a single impeller curve plotted as head versus flow. The point shown is inconsistent with the pump operation. Therefore, that pair of flow and pressure measurements is not validated and should not be used in the subsequent steps.

Validation versus Rectification The goal of both rectification and validation is the detection and identification of measurements that contain systematic error. Rectification is typically done simultaneously with reconciliation using the reconciliation results to identify measurements that potentially contain systematic error. Validation typically relies only on other measurements and operating information. Consequently, validation is preferred when measurements and their supporting information are limited. Further, prior screening of measurements limits the possibility that the systematic errors will go undetected in the rectification step and subsequently be incorporated into any conclusions drawn during the interpretation step.

INITIAL CONSTRAINT ANALYSIS AND ADJUSTMENTS

Spreadsheet Analysis Once validation is complete, prescreening the measurements using the process constraints as the comparison statistic is particularly useful. This is the first step in the global test discussed in the rectification section. Also, an initial adjustment in component flows will provide the initial point for reconciliation. Therefore, the goals of this prescreening are to:

- Pretreat raw measurements
- Estimate the overall and component constraint deviations
- Identify missing measurements
- Adjust (initially) the measurements to close the constraints

The principal focus of this validation is the material and energy bal-

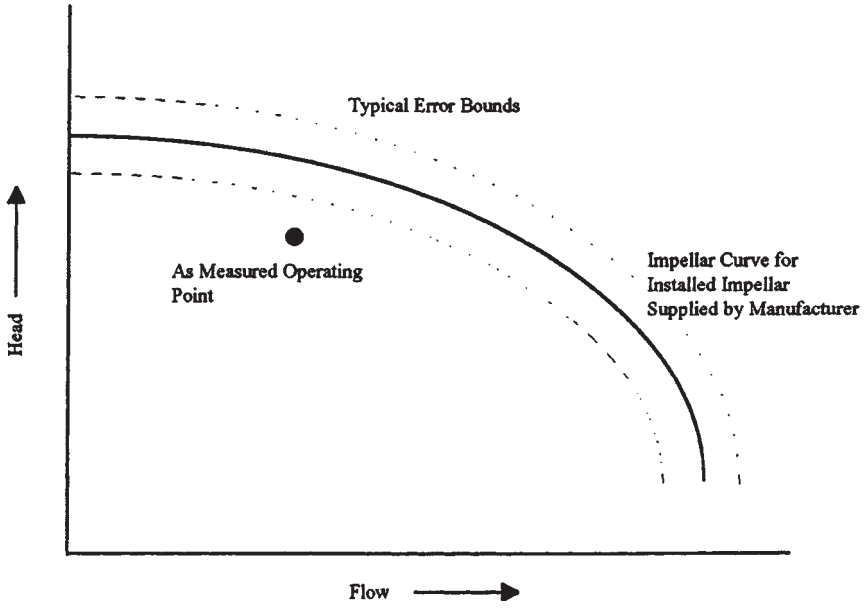


FIG. 30-16 Typical pump curve showing inconsistency between measurement and curve.

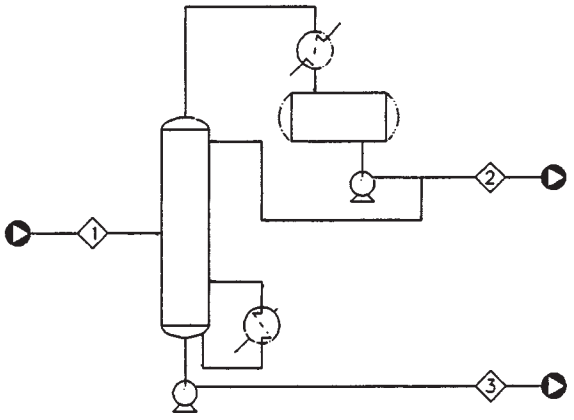


FIG. 30-17 Distillation tower example.

ances for the unit. Specifically designed spreadsheets are particularly useful during this step. The level of sophistication depends upon the analysts' goals. Spreadsheets can be used for pretreatment of measurements, constraint analysis, and measurement adjustment. Oftentimes, the more sophisticated reconciliation and rectification methods are not warranted or will not provide any better results, particularly when a single unit is under analysis.

For the purposes of this discussion, consider a single distillation tower with one feed, a distillate, and bottoms, as shown in Fig. 30-17.

A straightforward, generic analysis spreadsheet for this tower is shown in Fig. 30-18. For this example, the three stream compositions and the total flows have all been measured. Also, since this is a column in a purification train, the bottoms flow rate has been measured independently as the feed to the next tower.

Spreadsheet Structure There are three principal sections to the spreadsheet. The first has tables of as-reported and normalized composition measurements. The second section has tables for overall and component flows. These are used to check the overall and component material balance constraints. The third has adjusted stream and component flows. Space is provided for recording the basis of the adjustments. The structure changes as the breadth and depth of the analysis increases.

The example spreadsheet covers a three-day test. Tests over a period of days provide an opportunity to ensure that the tower operated at steady state for a period of time. Three sets of compositions were measured, recorded, normalized, and averaged. The daily compositions can be compared graphically to the averages to show drift. Scatter-diagram graphs, such as those in the reconciliation section, are developed for this analysis. If no drift is identified, the scatter in the measurements with time can give an estimate of the random error (measurement and fluctuations) in the measurements.

The second section of the spreadsheet contains the overall flows, the calculated component flows, and the material balance closure of each. The weighted nonclosure can be calculated using the random error calculated above, and a constraint test can be done with each component constraint if desired. Whether the measurement test is done or not, the nonclosure of the material balance for each component gives an indication of the validity of the overall flows and the compositions. If particular components are found to have significant constraint error, discussions with laboratory personnel about sampling and analysis and with instrument personnel about flow-measurement errors can take place before any extensive computations begin.

The measurements and flows can be adjusted to close the constraints. These adjustments can then be compared to the measurements to determine whether any are reasonable. Statistical routines or hand adjustments are possible. These adjusted flows and compositions might form the basis for the interpretation step bypassing any deeper reconciliation and rectification. This is particularly appropriate where many compositions are left unmeasured and those that are measured have different levels of error. More sophisticated routines will not compensate for incomplete, imprecise, and potentially inaccurate measurements.

Recommendations Once measurements are made, validation is the most important step for establishing a sound set of measurements. The comparisons against other measurements or other known pieces of information quickly identify suspect measurements. Spreadsheet analysis of constraints, particularly material and energy balances, identifies other weaknesses in the measurements and provides the opportunity for discussions with those responsible before considerable analysis effort is expended. Finally, initial adjustments provide the beginnings of the interpretation analysis.

RECONCILIATION

Single-Module Analysis Consider the single-module unit shown in Fig. 30-10. If the measurements were complete, they would consist of compositions, flows, temperatures, and pressures. These would contain significant random and systematic errors. Consequently, as collected, they do not close the constraints of the unit being studied. The measurements are only estimates of the actual plant operation. If the actual operation were known, the analyst could prepare a scatter diagram comparing the measurements to the actual values, which is a useful analysis tool. Figure 30-19 is an example.

If the measurements were completely accurate and precise (i.e., they contained neither random nor systematic error), all of the symbols representing the individual measurements would fall on the zero deviation line. Since the data do contain error, the measurements should fall within ±2 on this type of diagram. This example scatter diagram shows that some of the measurements do not compare well to the actual values.

Unfortunately, the actual plant operation is unknown. Therefore, the actual value of each of the measurements is unknown. The purpose of reconciliation is to adjust the measurements so that they close the process constraints. The implicit hypothesis is that the resultant adjusted measurements better represent the actual unit operation than do the actual measurements.

Statistical Approach Ignoring any discrepancies between the implicit model used to establish the constraints and the actual unit, the measurements are adjusted to close the constraints. This adjustment effectively superimposes the known process operation embodied in the constraints onto the measurements. Minimum adjustments are made to the measurements.

The matrix of measurements is rearranged into a stacked vector where each subsequent set of stream measurements follows the one above. As an example, the component flows in the $\mathbf{X}_1^m$ matrix are placed in the vector of measurements as follows:

$$\vec{\mathbf{X}}^m = \begin{bmatrix} x_{1,1} \\ x_{2,1} \\ \cdot \\ \cdot \\ x_{c,1} \\ x_{2,1} \\ \cdot \\ \cdot \\ x_{c-1,3} \\ x_{c,3} \end{bmatrix}$$

Defining, $$\delta\vec{\mathbf{X}}_1 = \hat{\vec{\mathbf{X}}}_1^m - \vec{\mathbf{X}}_1^m$$

Minimize: $$\delta\vec{\mathbf{X}}_1^{\mathrm{T}}\delta\vec{\mathbf{X}}_1$$

Such that: $$\vec{\mathbf{f}}(\hat{\vec{\mathbf{X}}}_1^m) = \vec{\mathbf{0}}$$

If the constraints are linear (e.g., the component flow material balances) or can be linearized, then

$$\mathbf{B}\hat{\vec{\mathbf{X}}}_1^m = \vec{\mathbf{0}}$$

In the material balance example, the matrix **B** contains the material balance coefficients for the component flows based on the implicit model of the process. These adjustments can be done by hand or by

ANALYSIS OF TOWER DATA

Measured compositions reported on lab logs

Component	Feed composition			Distillation composition			Bottoms composition		
	Date 1 wt%	Date 2 wt%	Date 3 wt%	Date 1 wt%	Date 2 wt%	Date 3 wt%	Date 1 wt%	Date 2 wt%	Date 3 wt%
Component 1 Component 2 Component 3 • • • Component c-1 Component c									
Total									

Average compositions for period

Component	Stream compositions		
	Feed wt%	Ovhd wt%	Btms wt%
Component 1 Component 2 Component 3 • • • Component c-1 Component c			
Total			

Normalized compositions for single date

Component	Stream compositions		
	Feed wt%	Ovhd wt%	Btms wt%
Component 1 Component 2 Component 3 • • • Component c-1 Component c			
Total			

Stream flowrates for single date

Stream	lb/hr	
Feed		
Distillate		
Bottoms		As measured
Bottoms		Back-calculated from next unit
Bottoms		Back-calculated to close

Projected stream flows—next tower basis

Component	Stream flows			Closure	
	Feed lb/hr	Ovhd lb/hr	Btms lb/hr	lb/hr	%
Component 1 Component 2 Component 3 • • • Component c-1 Component c					
Total					

Projected single date flows—next tower basis

Component	Stream flows			Closure	
	Feed lb/hr	Ovhd lb/hr	Btms lb/hr	lb/hr	%
Component 1 Component 2 Component 3 • • • Component c-1 Component c					
Total					

Possible material balance adjustment

Component	Stream flows						
	Feed		Ovhd product		Btms product		
	lb/hr	wt%	lb/hr	wt%	lb/hr	wt%	Descriptive notes
Component 1 Component 2 Component 3 • • • Component c-1 Component c							
Total							

FIG. 30-18 Generic spreadsheet for analyzing measurement validity.

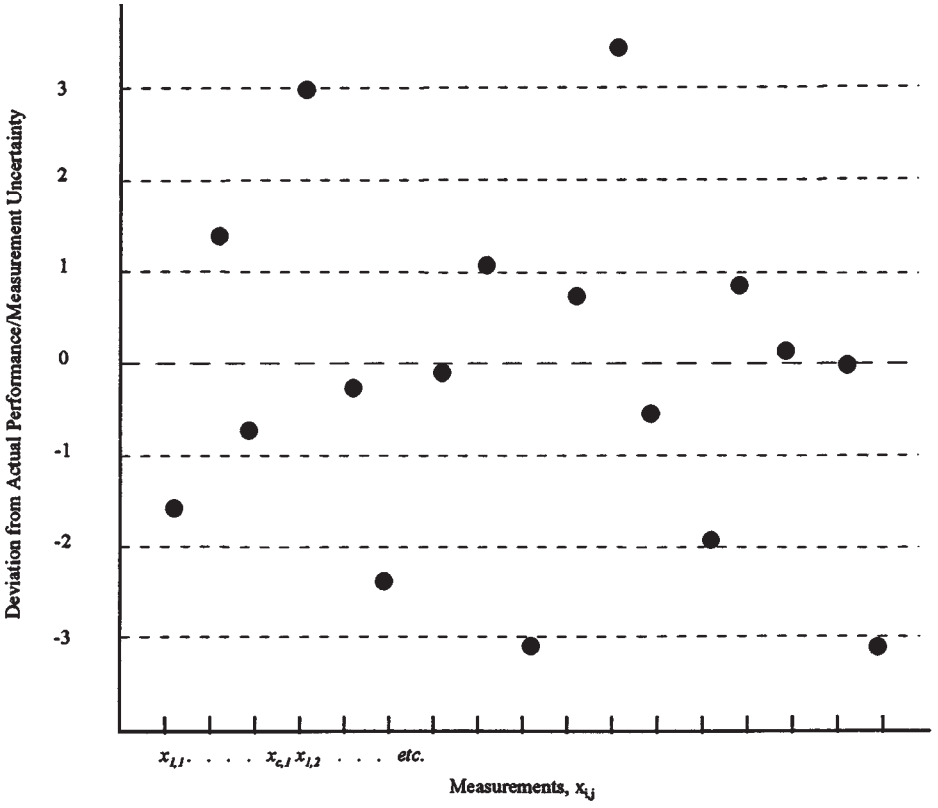


FIG. 30-19 Scatter diagram of measurements before reconciliation.

using computer aids. They can be made without consideration of measurement errors in the data (Leibovici, C.F., et al., "Improve Prediction with Data Reconciliation," *Hydrocarbon Processing*, October, 1993, 79–80) as above or can be done by accounting for the random errors (MacDonald, R.J. and C.S. Howat, "Data Reconciliation and Parameter Estimation in Plant Performance Analysis," *AIChE Journal*, **34**(1), 1988, 1–8.) For the latter, the problem becomes:

Minimize: $\delta\vec{\mathbf{X}}_1^{\mathrm{T}}\mathbf{J}^{-1}\delta\vec{\mathbf{X}}_1$

Such that: $\vec{\mathbf{f}}(\hat{\mathbf{X}}_1^m) = \vec{\mathbf{0}}$

where **J** is the variance-covariance of the measurements. If the number of measurements is limited for a stream, the adjustments can be made on the limited number of measurements. The constraints can also be used to estimate missing or discarded measurements: This use of the constraints is defined as *coaptation* in the literature. However, this propagates errors and should be done with caution.

Analysis of Measurement Adjustments Once reconciliation has been completed, the adjusted measurements can be compared to the actual measurements using a scatter diagram. Figure 30-20 presents an example. In this figure, the weighted residuals in the adjustments are plotted. The weighting factor is a measure of the random error in that particular measurement. In this visualization, the value of the residual should be between ± 2. The scatter has improved from the previous figure, but numerical studies have indicated that the analyst can expect only 60 percent of the measurements to be adjusted toward the actual value. Consequently, while the scatter may have improved, there is no guarantee that a particular adjusted measurement is better than the actual measurement. This is one of the principal shortcomings of any automatic data adjustment method.

Adjustments outside this range could be suspect, either because of measurement error or error in the estimated uncertainty. These will be evaluated in the rectification step. Weighted residual values of 0 do not necessarily indicate that the measurement is correct. While this is a possible explanation, a more likely one is that the selected constraints used in the reconciliation are not sensitive functions of this measurement. Therefore, in the interpretation step, caution is recommended in using these adjusted measurements to compare against the model estimate.

At this point, analysts have a set of adjusted measurements that may better represent the unit operation. These will ultimately be used to identify faults, develop a model, or estimate parameters. This automatic reconciliation is not a panacea. Incomplete data sets, unknown uncertainties and incorrect constraints all compromise the accuracy of the adjustments. Consequently, preliminary adjustments by hand are still recommended. Even when automatic adjustments appear to be correct, the results must be viewed with some skepticism.

Complex Flow Sheets Operating plants do not consist of single flashes, heat exchangers, distillation towers, or reactors. As the number of pieces of equipment increases within the unit under study, the reconciliation becomes more difficult. For example, Fig. 30-21 presents a more complicated, three-module unit.

There are now constraints for each of the modules within the unit. For example, the material and energy balances must close for each module. The overall material and energy balances must also close, but they are not independent. There are three approaches to close these constraints.

First, the reconciliation can be done separately around each module. Each module is studied alone. The measurements are reconciled to the individual module constraints without consideration of any other module with common streams. For example, the first module in the figure is reconciled, and the measurements corresponding to

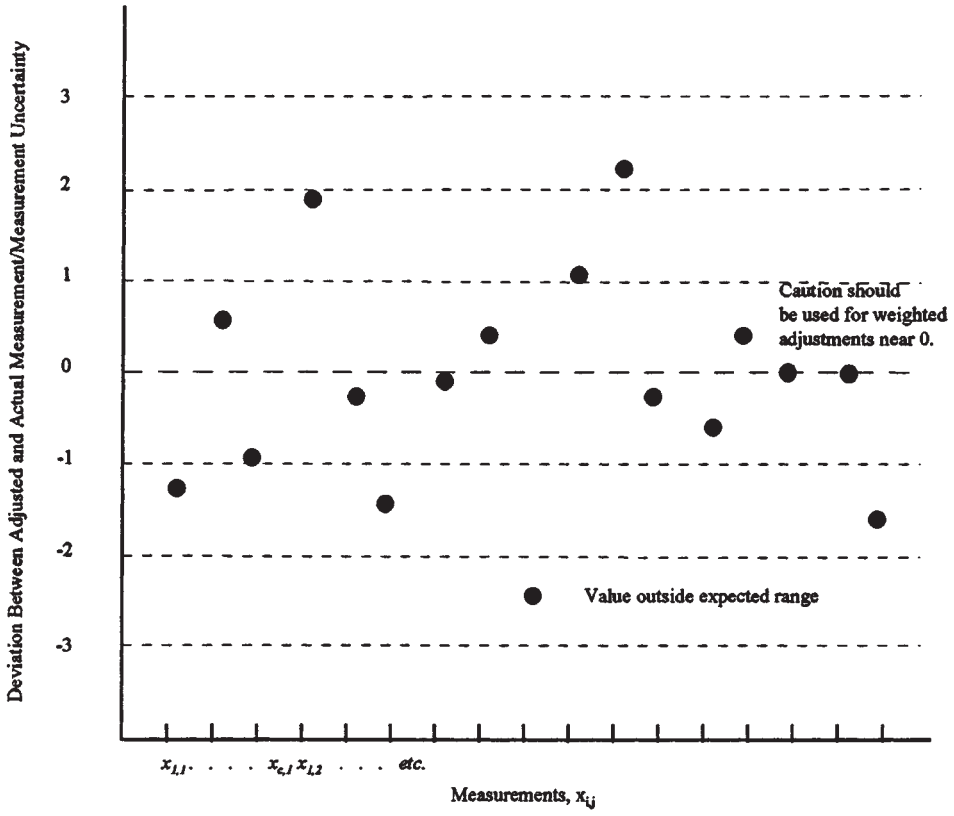


FIG. 30-20 Scatter diagram showing results of reconciliation.

stream 3 are adjusted to close the constraints around the first module. The reconciliation process moves to the second. The stream-3 measurements are adjusted again to close the module-2 constraints. This adjustment does not take into account any previous adjustments done for module 1. The adjustments will not be the same. The adjusted stream-3 compositions and flows will be different for module 1 and module 2. Consequently, the overall constraints will not close. This method provides the best estimate for the actual operation for a specific module, but each stream joining two units is reconciled twice yielding two differing estimates.

In the second approach, the reconciliation is done sequentially from module to module within the unit under study. This is done typically following the primary direction of material flow. This approach reconciles the measurements for each module in turn, progressing through the entire unit under study. Consequently, the reconciled measurements from the first module are used in the reconciliation of

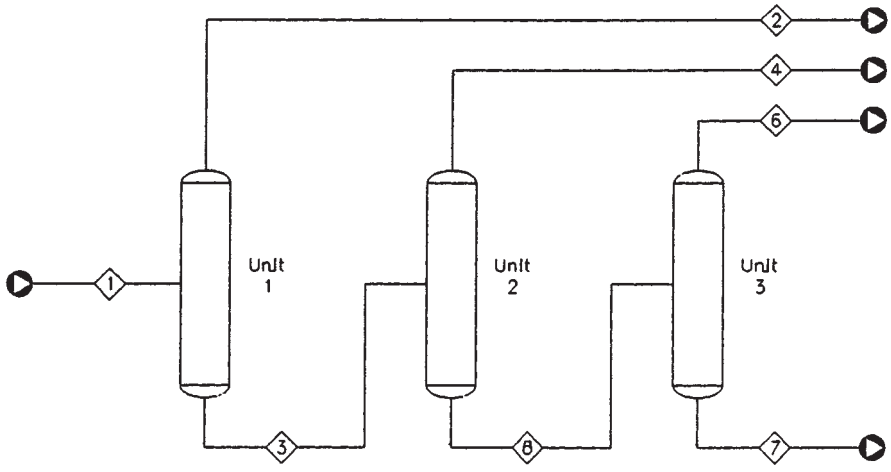


FIG. 30-21 Three-module unit.

the measurements for the second. Each stream is reconciled only once. This ensures overall closure upon completion. Errors in the reconciliation from the first are propagated to subsequent modules. Given that numerical studies of plant data show that the reconciliation methods only improve the estimate of actual performance 60–70 percent of the time, this method introduces significant errors that propagate to an ever greater extent as the complexity of the flow sheet increases. This method should be avoided.

In the third approach, the reconciliation is done simultaneously for all of the modules in the entire unit. This provides a consistent set of adjusted measurements for the entire flow sheet, ensuring individual module and entire unit constraint closure. However, each module's adjustments are poorer than those obtained by a separate reconciliation.

If the focus of the analysis is on an individual module or piece of equipment, the separate method is recommended.

References A variety of mathematical methods are proposed to cope with linear (e.g., material balances based on flows) and nonlinear (e.g., energy balances and equilibrium relations) constraints. Methods have been developed to cope with unknown measurement uncertainties and missing measurements. The reference list provides ample insight into these methods. See, in particular, the works by Mah, Crowe, and Madron. However, the methods all require more information than is typically known in a plant setting. Therefore, even when automated methods are available, plant-performance analysts are well advised to perform initial adjustments by hand.

Recommendations Plant measurements should be adjusted to close the constraints of the process. This adjustment should be done on a component or subcomponent (e.g., atomic) basis. The adjustments should be done recognizing (at a minimum) the uncertainty in the measurements. While sophisticated routines have been developed for reconciliation, the vagaries of plant measurements may make them unsuitable in most applications. The routines are no substitute for accurate, precise measurements. They cannot compensate for the uncertainties and limited information typically found in plant data.

RECTIFICATION

Overview Reconciliation adjusts the measurements to close constraints subject to their uncertainty. The numerical methods for reconciliation are based on the restriction that the measurements are only subject to random errors. Since all measurements have some unknown bias, this restriction is violated. The resultant adjusted measurements propagate these biases. Since troubleshooting, model development, and parameter estimation will ultimately be based on these adjusted measurements, the biases will be incorporated into the conclusions, models, and parameter estimates. This potentially leads to errors in operation, control, and design.

Some bias is tolerable in the measurements. This is the case when:

- The bias is insignificant compared to the random error
- The bias does not have significant impact on the measurement adjustment
- The bias does not contribute significantly to the errors in the constraints
- The biased measurement is of little value during interpretation

Consequently, these biases are not of concern.

However, other bias errors are so substantial that their presence will significantly distort any conclusions drawn from the adjusted measurements. *Rectification* is the detection of the presence of significant bias in a set of measurements, the isolation of the specific measurements containing bias, and the removal of those measurements from subsequent reconciliation and interpretation. Significant bias in measurements is defined as *gross error* in the literature.

The methods discussed in the technical literature are not exact. Numerical simulations of plant performance show that gross errors frequently remain undetected when they are present, or measurements are isolated as containing gross errors when they do not contain any.

Consequently, analysts must take a skeptical view of rectification results. The detection and isolation methods are computationally intensive and better suited for automatic procedures. Simulation studies show that the best interpretation occurs when entire measurement sets found containing gross errors are discarded. Therefore, the emphasis in this section is on detection. Citations are given for the detection and isolation of measurements containing gross errors.

Reconciliation Result The actual measurements do not close the constraint equations. That is,

$$\vec{\mathbf{f}}(\vec{\mathbf{X}}_1^m) \neq \vec{\mathbf{0}}$$

or, in the linear case,

$$\mathbf{B}\vec{\mathbf{X}}_1^m \neq \vec{\mathbf{0}}$$

Note that nonlinear constraints can be treated in this manner through linearization. Consequently, adjustments to the measurements are required. The result from the reconciliation process is this set of adjusted measurements,

$$\hat{\vec{\mathbf{X}}}_1^m$$

such that

$$\mathbf{B}\hat{\vec{\mathbf{X}}}_1^m = \vec{\mathbf{0}}$$

These were developed using constrained regression analysis or other suitable methods such that the following objective function is minimized.

$$\delta\vec{\mathbf{X}}_1^{\mathbf{T}}\mathbf{J}^{-1}\delta\vec{\mathbf{X}}_1$$

which can be expressed in algebraic form as:

$$\sum_i \left(\frac{\hat{x}_i^m - x_i^m}{\sigma_{x_i}}\right)^2$$

These adjusted measurements are examined as part of the rectification procedure.

There are three principal categories of rectification tests according to Mah (*Chemical Process Structures and Information Flows,* Butterworths, Boston, 1989, p. 414). These are the global test, the constraint test (nodal test), and the measurement test. There are variations published in the literature, and the reader is referred to the references for discussion of those.

Global Test The measurements do not close the constraints of the process. In the linear, material balance constraint example used above,

$$\mathbf{B}\vec{\mathbf{X}}_1^m = \vec{\mathbf{r}}$$

where $\vec{\mathbf{r}}$ is a vector of residuals for the constraints. The purpose of the global test is to test the null hypothesis:

$$H_0: \vec{\mathbf{r}} = \vec{\mathbf{0}}$$

$$H_a: \vec{\mathbf{r}} \neq \vec{\mathbf{0}}$$

The variance-covariance matrix for $\vec{\mathbf{r}}$ is:

$$\mathbf{R} = \mathbf{BJB}^{\mathbf{T}}$$

The test statistic

$$\mathbf{r}^{\mathbf{T}}\mathbf{R}^{-1}\mathbf{r}$$

is a chi-squared (χ^2) random variable with degrees of freedom equal to the number of constraints, assuming all measurements are made in the constraint equations.

This test does not require reconciliation before it is applied. However, should the null hypothesis be rejected, it only indicates that a gross error might be present. It does not isolate which of the measurements (or constraints) are in error. Consequently, gross-error isolation must be done subsequently.

Constraint Test In this test, each individual constraint is tested based on the measurements. The test statistic is

$$\frac{r_j}{\sqrt{R_{jj}}}$$

with

$$H_0: r_j = 0$$

$$H_a: r_j \neq 0$$

This statistic is normal. As with the global test, the constraint test is based on the actual measurements before reconciliation. Reconciliation is not required in advance of the application of this test. Also, the

constraint test does not isolate which of the measurements contains gross error. Subsequent isolation is required.

Measurement Test This test compares the adjusted measurements to the actual measurements. In so doing, each measurement is tested for gross error. From the reconciliation development,

$$\delta\vec{\mathbf{X}}_1 = \hat{\vec{\mathbf{X}}}_1^m - \vec{\mathbf{X}}_1^m$$

where the vector $\delta\vec{\mathbf{X}}_1$ is the adjustments made to each of the measurements. Premultiplying this vector by the inverse of the variance-covariance matrix of the measurements gives a test of maximum power (assuming that **J** is diagonal). Define,

$$\vec{\mathbf{d}} = \mathbf{J}^{-1}\delta\vec{\mathbf{X}}_1$$

Define the variance-covariance matrix for this vector to be

$$\mathbf{Q} = \mathbf{B}^{\mathrm{T}}(\mathbf{B}\mathbf{J}\mathbf{B}^{\mathrm{T}})^{-1}\mathbf{B}$$

Thus, the $N(0,1)$ test statistic is

$$\frac{|d_j|}{\sqrt{Q_{jj}}}$$

Unlike the other two tests, this is associated with each measurement. Reconciliation is required before this test is applied, but no further isolation is required. However, due to the limitations in reconciliation methods, some measurements can be inordinately adjusted because of incorrectly specified random errors. Other adjustments that do contain gross errors may not be adjusted because the selected constraints are not sensitive to these measurements. Therefore, even though the adjustment in each measurement is tested for gross error, rejection of the null hypothesis for a specific measurement does not necessarily indicate that that measurement contains gross error.

Gross-Error Isolation Gross-error detection methods do not isolate which measurements contain gross error. The Global and Constraint Tests work only with the process constraints. While they detect gross errors in one or more constraints, they do not isolate the measurements. The measurement test does isolate those measurements that were adjusted to a larger-than-expected extent. These adjustments may be in error, as discussed above. Once the presence of gross errors has been detected, the actual measurements need to be isolated. Rosenberg et al. (Rosenberg, J., R.S.H. Mah, and C. Iordache, "Evaluation of Schemes for Detecting and Identifying Gross Errors in Process Data," *Industrial and Engineering Chemistry, Research,* **26**(3), 1987, 555–564) review methods for isolation of gross errors.

The authors test two methods coupled with the measurement test. In one, they sequentially eliminate measurements and rearrange the constraints to isolate the specific measurements that contain gross errors. In the other, streams are added back as the search continues.

Both of these schemes require substantial computing effort and are focused on networks of modules (i.e., complex units). The reader is referred to the article for the details of these isolation procedures as they are beyond the scope of this section.

Statistical Power There are two types of errors. In the type-I error, gross errors are isolated as present when none are. In the type-II error, no errors are isolated when they are actually present. A third measure of error is selectivity taken from Rosenberg et al. (cited above), which is the normalized probability of detecting a gross error in a stream when there is error in that stream only. The power of the detection methods is defined as the probability of detecting gross errors when present. The probability of making a false detection must be minimized. The selectivity should also be high. A balance among these competing goals must be established.

Results of simulation studies of different types of flow sheets and measurement-error levels show that the performance of these schemes depends on the magnitude of the gross error relative to the measure of the random error. The larger the gross error, the greater the power and lower the probability of committing a type-II error. The complexity of the flow sheet contributes in the form of the constraint equations. Flowsheets with parallel streams have identical constraint equations, giving equal statistical performance. For the cases studied, the power ranges from 0.1 to 0.8 (desired value 1.0), the probability of making type-II errors ranges from 0.2 to 0.7 (desired value 0.0), and the selectivity ranges from 0.1 to 0.8 (desired value 1.0). These statistics depend on random and gross error magnitudes and flow sheet configuration. These ranges of statistics show that the tests are not exact.

This inexact performance leads to the recommendation that measurement sets should be discarded in their entirety when gross errors are detected. Therefore, actual isolation of which measurements contain error is not necessary when entire sets are discarded.

Recommendation When all measurements were recorded by hand, operators and engineers could use their judgment concerning their validity. Now with most acquired automatically in enormous numbers, the measurements need to be examined automatically. The goal continues to be to detect correctly the presence or absence of gross errors and isolate which measurements contain those errors. Each of the tests has limitations. The literature indicates that the measurement test or a composite test where measurements are sequentially added to the measurement set are the most powerful, but their success is limited. If automatic analysis is required, the composite measurement test is the most direct to isolation-specific measurements with gross error.

However, given that reconciliation will not always adjust measurements, even when they contain large random and gross error, the adjustments will not necessarily indicate that gross error is present. Further, the constraints may also be incorrect due to simplifications, leaks, and so on. Therefore, for specific model development, scrutiny of the individual measurement adjustments coupled with reconciliation and model building should be used to isolate gross errors.

INTERPRETATION

Overview Interpretation is the process for using the raw or adjusted unit measurements to troubleshoot, estimate parameters, detect faults, or develop a plant model. The interpretation of plant performance is defined as a discreet step but is often done simultaneously with the identification of hypotheses and suitable measurements and the treatment of those measurements. It is isolated here as a separate process for convenience of discussion.

The activities under interpretation are divided into four categories. Troubleshooting is a procedure to identify and solve a problem in the unit. Hypothesized causes for the observed problems are developed and then tested with appropriate measurements or identification of changes in operating conditions.

Parameter estimation is a procedure for taking the unit measurements and reducing them to a set of parameters for a physical (or, in some cases, relational) mathematical model of the unit. Statistical interpretation tempered with engineering judgment is required to arrive at realistic parameter estimates. Parameter estimation can be an integral part of fault detection and model discrimination.

Fault detection is a monitoring procedure intended to identify deteriorating unit performance. The unit can be monitored by focusing on values of important unit measurements or on values of model parameters. Step changes or drift in these values are used to identify that a fault (deteriorated performance in unit functioning or effectiveness) has occurred in the unit. Fault detection should be an ongoing procedure for unit monitoring. However, it is also used to compare performance from one formal unit test to another.

Model discrimination is a procedure for developing a suitable description of the unit performance. The techniques are drawn from the mathematics literature where the goodness-of-fit of various proposed models are compared. Unfortunately, the various proposed models will usually describe a unit's performance equally well. Model discrimination is better accomplished when raw or adjusted measurements from many, unique operating conditions provide the foundation for the comparisons.

These procedures are not mutually exclusive and are divided here as a matter of convenience for discussion. The identification, measurement treatment, and interpretation are typically embodied into a single effort with testing and retesting as analysts search for the cause of the observed symptoms.

Troubleshooting The initial steps of troubleshooting have been discussed in the identification section. Successful troubleshooting

requires the acquisition and organization of a large amount of observations from diverse sources. Analysts rely heavily on the observations of operators and supervisors along with the interpretation of unit measurements. In troubleshooting, a complete unit test is usually the last resort to identify the cause of the observed problem. Therefore, the measurements and observations are usually incomplete, and analysts must hypothesize causes, identify measurements or alternative operating conditions, and interpret the results based on the analysts' understanding of the unit operation.

Hasbrouck et al. (Hasbrouck, J.F., J.G. Kunesh, and V.C. Smith, "Successfully Troubleshoot Distillation Towers," *Chemical Engineering Progress,* March 1993, 63–72) provide guidelines for those practicing troubleshooting. These have been incorporated into much of the preparation and identification discussion. Analysts must understand the objectives of the troubleshooting activities established by unit supervision, plant management, and the analysts' management. Analysts must be able to communicate with and have the cooperation of the unit operators and supervision. Analysts must understand the unit. Discussions with operators and supervision should emphasize the symptoms and not their conclusions. Analysts should observe unit operation both in the control room and in the unit to establish whether the observations of those involved are accurate. Analysts should obtain log-sheet measurements to provide the foundation for establishing the hypotheses explaining the unit problems. As part of this collection, log sheets from a period when the unit operated correctly should also be obtained. At this point, the interpretation process can begin.

The current and past operation should be compared so that the timing of the observed problems is established. The possible causes (hypotheses) can be compared against the measurements found on the log sheets. The number of possible causes can then be reduced. When the quantity or quality of measurements is insufficient to further reduce the set of causes, additional measurements are required. These may require special instruments (e.g., gamma-ray scanning) not routinely used in the plant. Alternative operating conditions may also be required to further reduce the number of causes. As part of the problem identification, it is always important to look for measurements that are inconsistent with the proposed explanation. They will be more informative than the ones justifying the hypothesized cause. Ultimately, with appropriate additional measurements, the cause can be identified. This is not an exact science and, as stated above, relies heavily upon the communication, technical, and investigative skills of analysts.

Figure 30-22 is an expanded flowchart for troubleshooting activities incorporating the recommendations for hypothesis development as well as interpretation laid out in Table 30-1. The figure is adapted from Hasbrouck et al. but expanded and rearranged to make it germane to units beyond distillation. Following the guidelines from Table 30-1, the changes in the unit equipment, instrumentation, and operating conditions that coincide with the observed problems are listed. Instrument readings are verified to ensure that the problem is valid and not an aberration of poor instruments or calibrations. Hasbrouck et al. recommend establishing the magnitude of the problem and verifying that it is significant enough to justify further troubleshooting activities. In this step, analysts monitor unit operations to verify the observations of operators and unit supervisors. Hypothesis development continues with establishing whether the problem is with the unit under study or with an upstream unit, downstream unit, auxiliary equipment, or control. If it is outside the unit under study, attention should turn to troubleshooting that equipment. If it is within the unit, then analysts should establish whether the operating conditions are inappropriately set, causing capacity or efficiency problems, or whether the equipment itself is the cause of the problem. Troubleshooting continues by acquiring measurements from logs or, if necessary, from special instrumentation to reduce the number of possibilities and ultimately identify the cause of the problems. The process concludes with the alternative operating conditions or equipment identified with supporting economic justification. Analysts then communicate the results to the management, unit supervision, and the operators. If necessary, the analysts oversee the implementation of the changes.

Figure 30-22 should be interpreted as a guideline for successful troubleshooting and not a recipe to be followed exactly. Any one of the steps can be bypassed as the ground rules for the activity dictate and the insight into the problem develops. Since troubleshooting is not an exact science, analysts are well advised to look always for the alternative causes recognizing that symptoms' underlying causes are not unique.

Parameter Estimation Relational and physical models require adjustable parameters to match the predicted output (e.g., distillate composition, tower profiles, and reactor conversions) to the operating specifications (e.g., distillation material and energy balance) and the unit input, feed compositions, conditions, and flows. The physical-model adjustable parameters bear a loose tie to theory with the limitations discussed in previous sections. The relational models have no tie to theory or the internal equipment processes. The purpose of this interpretation procedure is to develop estimates for these parameters. It is these parameters linked with the model that provide a mathematical representation of the unit that can be used in fault detection, control, and design.

The purpose is to develop estimates of significant model parameters that provide the best estimate of unit operation. The unit operation is embodied in the measurements.

$$\vec{\mathbf{X}}_1^m$$

If reconciliation and rectification procedures were applied to the measurements, either statistically or judgmentally, to close the constraints, the unit operation is also embodied in the adjusted measurements.

$$\hat{\vec{\mathbf{X}}}_1^m$$

Each of these have corresponding uncertainties.

The object, then, is to develop a set of predicted values for the measurements based on the model

$$\hat{\vec{\mathbf{X}}}_1^M$$

such that the differences between these model predictions and the raw or adjusted measurements are minimized.

Define: $$\delta\vec{\mathbf{X}}_1^M = \hat{\vec{\mathbf{X}}}_1^M - \vec{\mathbf{X}}_1^m$$

or $$\delta\vec{\mathbf{X}}_1^M = \hat{\vec{\mathbf{X}}}_1^M - \hat{\vec{\mathbf{X}}}_1^m$$

and minimize: $$\delta\vec{\mathbf{X}}_1^{M\mathrm{T}}\delta\vec{\mathbf{X}}_1^M$$

This minimization can be unweighted as above, or it can be weighted using the statistical uncertainty $\mathbf{J}^{-1}$ with respect to the measurements or engineering judgment.

While the statistical weighting is elegant and rigorous if the uncertainties are known, its applicability is limited because the uncertainties are seldom known. Commercial simulator models are yet unable to iterate on the parameter estimates against the unit measurements. And, the focus should be on a limited subset of the complete measurements set.

The parameter adjustment procedure is most often done with analysts performing the adjustments by comparing model predictions to the raw or adjusted measurements. The spreadsheet given in Fig. 30-18 is extended to include comparisons between the predictions and basis. Figure 30-23 presents one possible extension. The spreadsheet contains two principal sections. First, there is a section for the comparison of component flows. The component flows for the comparisons are the raw or adjusted measurements. The predicted values come from the model with the current estimates for the parameters. The deviations are summarized as a root mean square error between the measurements and predictions, weighted if appropriate. The second section includes a comparison between measured and predicted values that are of particular interest, like the measurements upon which the operators focus, trace component concentrations, ratios of one group of components to another, or a special product. This section of the spreadsheet is repeated as often as necessary to provide a running comparison, as the parameter values are adjusted to improve the description of the unit operation. The adjustment of the parameter values is accomplished through finite-difference approximation of the sensitivity of the performance criteria to the parameter values.

The hurdles to arriving at a unique set of parameter values are large.

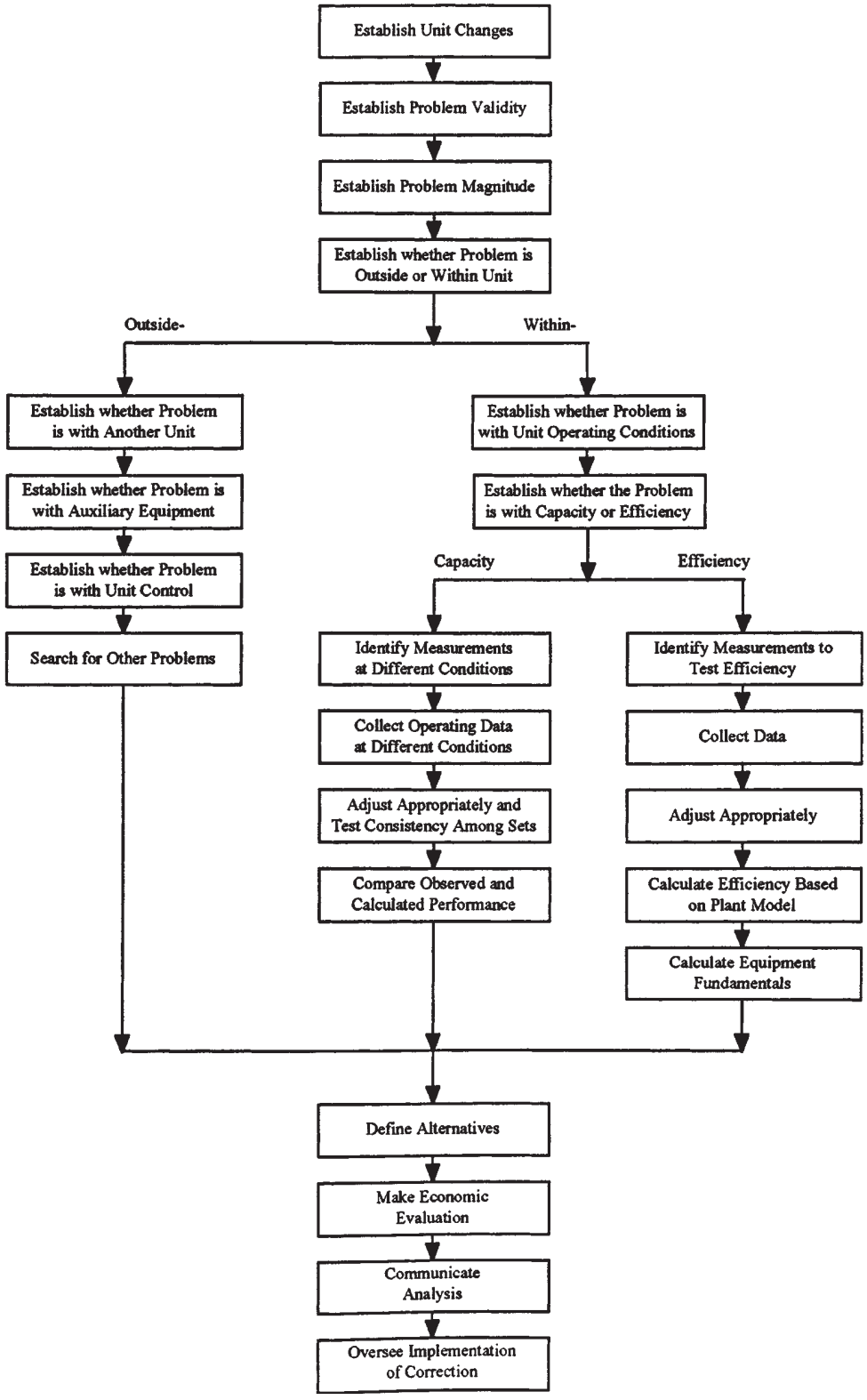


FIG. 30-22 Flowchart for troubleshooting.

Comparison between plant and calculated material balance for tower

Component	Stream flows								
	Feed, lb/hr			Ovhd product, lb/hr			Btms product, lb/hr		
	Plant	Calc	Δ (Delta)	Plant	Calc	Δ (Delta)	Plant	Calc	Δ (Delta)
Component 1 Component 2 Component 3 • • • Component c-1 Component c									
Total									

RMSE lb/hr lb/hr
RMSE % %

	Plant	Calc
Temperatures Overhead, F Bottoms, F		
Duties MM Btu/hr		
Targets Target 1 Target 2 Target 3		

FIG. 30-23 Spreadsheet extension to Fig. 30-17 to compare measurements or adjusted measurements to predicted values.

• *The measurements do not close the constraints.* Estimation of the parameter values against the actual measurements results in parameter values that are not unique.

• *The adjusted measurements are not unique and may be no better than the actual measurements.* Simulation studies testing reconciliation methods in the absence of gross error show that they arrive at a better estimate of the actual component and stream flows 60 percent of the time; 40 percent of the time, the actual measured values better represent the unit performance.

• *Gross-error-detection methods detect errors when they are not present and fail to detect the gross errors when they are.* Coupling the aforementioned difficulties of reconciliation with the limitations of gross-error-detection methods, it is likely that the adjusted measurements contain unrecognized gross error, further weakening the foundation of the parameter estimation.

• *Few simulation studies of parameter estimation in analysis of plant-performance are given in the literature.* Those that are reported show that, for the levels of measurement errors expected in a plant, the uncertainty in estimated parameter values is very large, much larger than that needed for design. For example, MacDonald and Howat (1988) show that, for a simple flash vessel with an actual simulated value of 75 percent flash efficiency, the 95 percent confidence interval in the interpretation of simulated operation is 75% ± 12%. Verneuil et al. (1992) point out that interpretation of unit data using highly nonlinear models should be done with the recognition that the results must be treated as an approximation.

• *The presence of errors within the underlying database further degrades the accuracy and precision of the parameter estimate.* If the database contains bias, this will translate into bias in the parameter estimates. In the flash example referenced above, including reasonable database uncertainty in the phase equilibria increases the 95 percent confidence interval to ±14. As the database uncertainty increases, the uncertainty in the resultant parameter estimate increases as shown by the trend line represented in Fig. 30-24. Failure to account for the database uncertainty results in poor extrapolations to other operating conditions.

• *The models that require parameter estimates are approximate.* Much of the theoretical basis of the parameter definition is lost. Equipment nonlinearities and boundaries are not accounted for in the analysis.

Despite these hurdles, models with accurate parameter estimates are required for analysis, control, and design. The effectiveness of parameter estimation can be improved by following these guidelines.

• *Increase the number of measurements included in the measurement set by using measurements from repeated sampling.* Including repeated measurements at the same operating conditions reduces the impact of the measurement error on the parameter estimates. The result is a tighter confidence interval on the estimates.

• *Include measurements that represent the internal conditions of equipment.* Including internal measurements such as tray compositions, between-catalyst-bed measurements or spatial measurements in a CSTR improve the likelihood that the parameter estimates are accurate. These measurements are particularly useful when product compositions (e.g., principal component composition in superfractionation) are not a sensitive measure of the parameter estimate.

• *Increase the number of operating conditions in the measurement set.* Measurement sets from different operating conditions have the same effect as increasing the number of measurements. They have the added benefit identifying weaknesses in the model when it cannot accurately describe all of the conditions.

• *Focus on specific measurements of particular sensitivity during the parameter adjustment.* Analysts should focus on the primary measurements upon which the operation, control, or design are based during the parameter adjustment step. This guideline suggests the artificial weighting of particular measurements. For example, in superfractionation, the nondistributed component product compositions provide little insight into evaluating the accuracy of the estimate of the tray efficiency. Including the deviation in these when developing a new parameter estimate provides little value and potentially masks the impact that the parameters have on the trace component compositions. Monitoring the deviations in the internal tray compositions of these nondistributed components in the region where they drop from the feed-tray composition to zero composition is important, but it is not where these compositions are at their limiting values on the other side of the feed tray.

• *Use additional measurement sets that were not included in the development of the parameter estimates to test their accuracy.* A certain subset of the raw or adjusted measurements is used to adjust the parameter estimate. Once the optimal values are attained, the model is used to predict values to compare against other measurement sets or subsets. These additional measurements provide an independent check on the parameter estimates and the model validity.

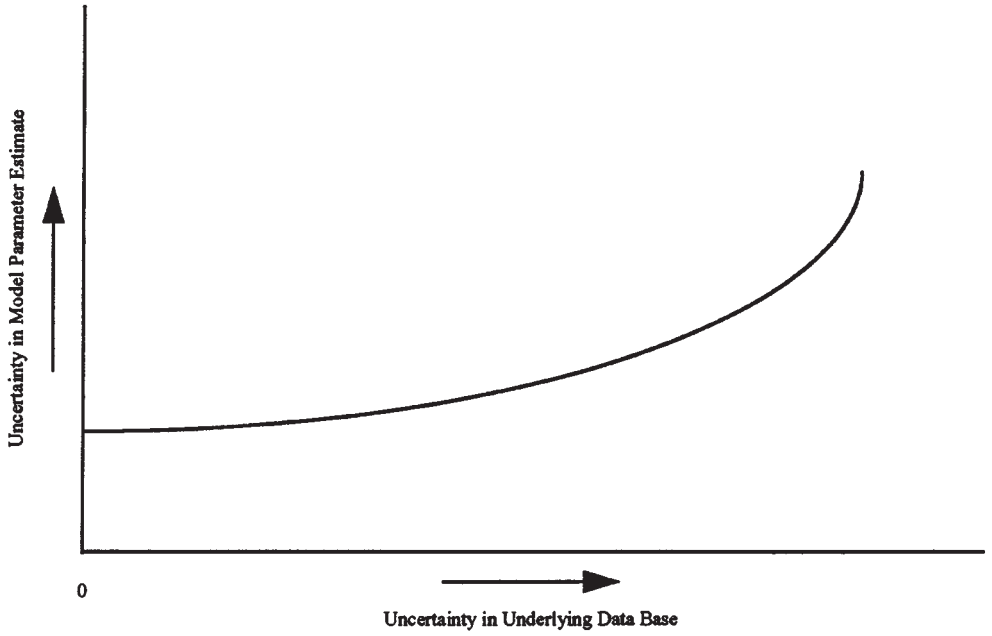


FIG. 30-24 Trend in parameter estimate uncertainty as the database uncertainty increases.

As with troubleshooting, parameter estimation is not an exact science. The facade of statistical and mathematical routines coupled with sophisticated simulation models masks the underlying uncertainties in the measurements and the models. It must be understood that the resultant parameter values embody all of the uncertainties in the measurements, underlying database, and the model. The impact of these uncertainties can be minimized by exercising sound engineering judgment founded upon a familiarity with unit operation and engineering fundamentals.

Fault Detection Measurements for units operating at steady-state fluctuate around mean values. The means tend to drift with time. Dynamic processes necessarily have time fluctuations in the measurements. These fluctuations and drifts make it difficult to determine readily the level of unit performance. Along with the process measurements, utility, raw material, and catalyst usage are monitored through the course of operation. The efficiency or economics of the unit are strong functions of these usages. These too change with time, and it is difficult to determine if the efficiency of the unit operation has changed. Control of the unit depends upon the accuracy of unit instrument readings. Should the instruments deteriorate, input signals to the controllers deteriorate and consequently control actions deteriorate. The validity of the instrument readings must be monitored to ensure that readings and the resultant actions are appropriate for efficient control.

These observations lead to the principal questions toward which fault detection is addressed.

- Has the unit operation effectiveness changed due to the input conditions, ambient conditions, or the state of the equipment?
- Has the unit operation efficiency deteriorated resulting in poorer performance?
- Has one or more of the instruments deteriorated such that the readings no longer represent the unit operation?

A fault may interfere with the effectiveness or the functioning of the unit (Watanabe, K., and D.M. Himmelblau, "Incipient Fault Diagnosis of Nonlinear Processes with Multiple Causes of Faults," *Chemical Engineering Science,* **39**(3), 1984, 491–508). The first question addresses the effectiveness. The second two address the functioning. Fault detection is a unit monitoring activity, done automatically or periodically, to determine whether the unit operation has changed.

Figures 30-11 through 14 provide typical traces of unit operations. Figure 30-12 shows a drift in the measurement, but it does not readily justify a conclusion that the unit operation is changing from one state to another. The apparent step changes shown in Fig. 30-13 may be due to instrument failure, input changes to the unit, operator-induced changes, and an aberration of the chart scaling. It is not readily clear whether the unit functioning or effectiveness has changed in either of these traces. The complex interactions defined by the chemical engineering and equipment fundamentals within the unit appear as changes in the measurements. The changes do not necessarily mean that the functioning or effectiveness of the unit has changed in any significant way.

The purpose of fault detection is to interpret the set of measurements to determine whether the operation of the unit has changed. This interpretation is done by monitoring the set of the measurements or by monitoring values for the significant unit parameters. It is done automatically as part of the computer control of the unit or periodically as when comparing one unit test to a subsequent one.

Automatic fault detection and diagnosis relies upon the interpretation of the unit measurements as they are gathered by the computer control/data acquisition system. The goal is to identify faults before they jeopardize the unit operation that could ultimately pose product, equipment, and safety problems if they are not corrected. The difficulty is that high-frequency data acquisition systems obtain a large amount of measurements. Automatic filtering methods and data compression are required to retain the unit trends without treating and archiving all the measurements. Readers are referred to Watanabe and Himmelblau (Watanabe, K. and D.M. Himmelblau, "Incipient Fault Diagnosis of Nonlinear Processes with Multiple Causes of Faults," *Chemical Engineering Science,* **39**(3), 1984, 491–508) and their citation list for a discussion of filtering methods. Narashimhan et al. propose that recording and analysis be done only when the process steady state has changed (Narashimhan, S., R.S.H. Mah, A.C. Tamhane, J.W. Woodward, and J.C. Hale, "A Composite Statistical Test for Detecting Changes of Steady States," *AIChE Journal,* **32**(9), 1986, 1409–1418). They develop a method for testing whether the unit is in steady state.

Periodic fault detection is readily done by analysts without extensive software support. Process monitoring such as the examination of the traces discussed above are one example. However, the number of measurements in a single set have such complex interactions that it is

difficult to determine whether the unit operation has changed. A better approach for periodic fault detection is to estimate the parameter values based on the measurements. The parameters, assuming that the model is accurate, embody the entire operation of the unit as well as the uncertainties in the measurements. Since their number is small for any unit, it is easier to monitor the parameter values. Figure 30-25 presents a typical trend in unit parameter values. Two difficulties arise with this approach, however.

First, the parameter estimate may be representative of the mean operation for that time period or it may be representative of an extreme, depending upon the set of measurements upon which it is based. This arises because of the normal fluctuations in unit measurements. Second, the statistical uncertainty, typically unknown, in the parameter estimate casts a confidence interval around the parameter estimate. Apparently, large differences in mean parameter values for two different periods may be statistically insignificant.

A change in the measurements or parameters indicates a change in the unit operation. The diagnosis (interpretation) of the cause for the change requires troubleshooting skills.

Watanabe and Himmelblau (1984) present a discussion of their simulation studies of the dehydrogenation of heptane to toluene. Incomplete reaction, deterioration of catalyst performance, and fouling the heat exchange surface are specified as the source of the faults. These manifest themselves in the outlet concentration of toluene, the values of the Arrhenius equation frequency factor and activation energy, and the heat-transfer coefficient, respectively. If the toluene concentration falls, the reaction completion has decreased. If the frequency decreases and the activation energy increases, the catalyst has chemically degraded. If the frequency decreases with no change in the activation energy, the catalyst has physically degraded. If the heat-transfer coefficient decreases, the exchanger has fouled. They note, however, that model-formulation difficulties will mask problems such that the problems do not appear as symptoms in the parameter values.

Wei (Wei, C.-N., "Diagnose Process Problems," *Chemical Engineering Progress,* September 1991, 70–74) discusses his success in monitoring production rates and selectivity to identify faults in a moving bed adsorber. Continuous monitoring resulted in a time trace of values for his parameters, clearly indicating that the operation had changed. The cause of the change in the parameter values was then diagnosed using troubleshooting methods discussed above. It is important to be able to compare operation before and after control, equipment, and other unit modifications. The history of the parameter values provides valuable insight into the effectiveness of the modifications.

In Fig. 30-25, representation of the fault detection monitoring activity, there appears to be two distinct time periods of unit operation with a transition period between the two. The mean parameter value and corresponding sample standard deviation can be calculated for each time. These means can be tested by setting the null hypothesis that the means are the same and performing the appropriate *t*-test. Rejecting the null hypothesis indicates that there may have been a shift in operation of the unit. Diagnosis (troubleshooting) is the next step.

When the number of measurement sets is substantially less than that indicated Fig. 30-25, the interpretation becomes problematic. One option is to use the parameter values from one period to describe the measurements from another. If the description is within measurement error, the operation has not changed. If there is a substantial difference between the predictions and the measurements, it is likely that the operation has changed. Methods such as those developed by Narasimhan et al. (1986) can be used when the number of measurements are large. When implementing automatic methods to treat a large number of measurements, analysts should ensure that the unit is at steady state for each time period.

Model Discrimination Relational and physical models should be robust (i.e., able to describe the operation of the unit over a reasonable range of operating conditions). Relational models used in control do not necessarily describe the operation exactly. At any given operating condition, they exhibit bias from the actual operation. However, their intended purpose is to predict accurately trends in response to operating specification changes or deviations from setpoints. Physical models, particularly those used in incipient fault detection and diagnosis, must be unbiased, accurately reflecting the unit operation.

The parameters of these models must also be unique for the unit. Only one set of parameters should describe the operation over a wide range.

The models must be considered to be approximations. Therefore, the goals of robustness and uniqueness are rarely met. The nonlinear nature of the physical model, the interaction between the database and the parameters, the approximation of the unit fundamentals, the equipment boundaries, and the measurement uncertainties all contribute to the limitations in either of these models.

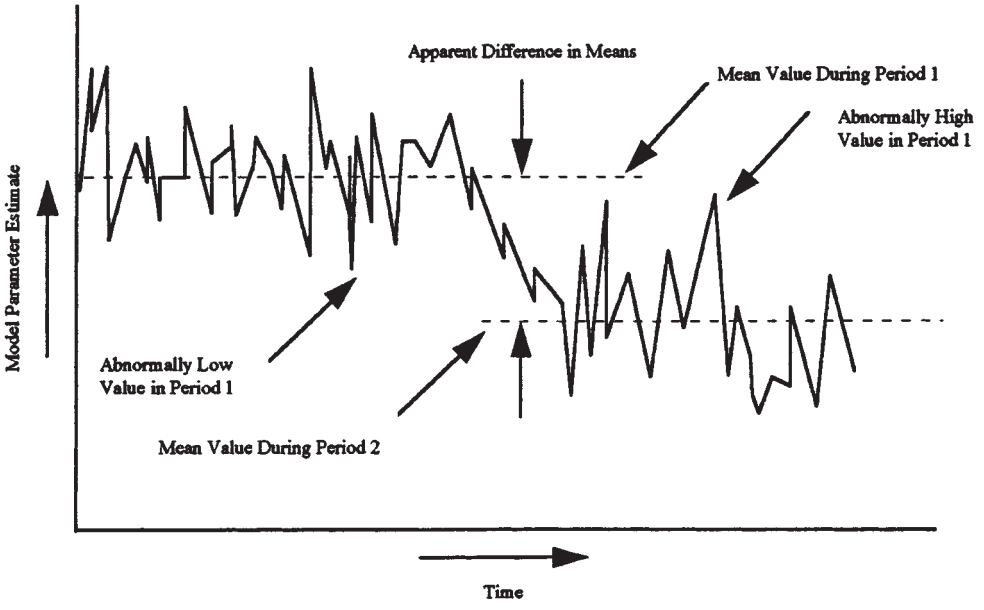


FIG. 30-25 Trend in model parameter developed during fault detection parameter estimation.

Because of these limitations, different models may appear to describe the unit operation equally well. Analysts must discriminate among various models with the associated parameter estimates that best meet the end-use criteria for the model development. There are three principal criteria for judging the suitability of one model over another. In addition, there are ancillary criteria like computing time and ease of use that may also contribute to the decision but are not of general concern.

The three principal criteria in order of importance are:

- Chemical engineering and equipment fundamentals foundation within the model
- Interpolation and extrapolation performance to other operating conditions
- Statistical representation of the raw or adjusted measurements

These criteria form the guidelines for discriminating among competing models. The principal reason for developing a model of the unit operation is to reliably predict unit performance under different operating conditions. Troubleshooting, fault detection, control, and design all fall under this purpose for developing a model. Different levels of accuracy may be required for each of these activities based on the end use criteria, but the choice of model within one of these activities should be that which best describes the unit operation. Models of limited accuracy have been used for operation and design with disappointing results. The developer of the model may recognize the model's limitations, but frequently these are not passed along to other analysts. Accurate predictions under different operating conditions is the primary goal and the foundation for the guidelines.

- The model that best describes the chemical engineering fundamentals including transport phenomena, rate mechanisms, and the thermodynamics; and includes contributions due to equipment nonlinearities and boundary conditions should be the model of choice.

This guideline is paramount. If the model is accurate in its fundamentals and equipment performance description, it should be able to describe the unit operation over a wide range of conditions. Its only limitations are the weaknesses of underlying database used in the model calculations and the errors in the unit measurements upon which the parameter estimates are based. An accurate description of the chemical engineering fundamentals incorporating the equipment nonlinearities with theory-based adjustable parameters is difficult to obtain. Analysts' knowledge of the transport and rate mechanisms is approximate under the best of circumstances. When the fundamentals are known, the mathematics may be so complex as to make the model unusable in the plant setting. Unless the model is specially developed for the analysis of plant performance, commercial simulators with their inherent inflexibility and limitations must be relied upon. They rarely allow changes to their model structure and do not incorporate the nonlinearities of equipment performance. Consequently, the model that is the best approximation of the fundamentals and equipment limitations and is computationally tractable should be the choice. It should have the greatest likelihood for extrapolation to other operating conditions.

- The model that best describes operating conditions other than those upon which its parameter estimates are based; i.e., the model that best interpolates among and extrapolates from its development conditions, should be the model of choice.

The best test for the suitability of the models is to develop their respective parameter estimates at one set of conditions and then test the accuracy of the models using measurements for other sets of conditions. The other conditions can be as relatively close to those used to establish the parameter estimates as might be experienced in routine operations. They may also be far different with different feed conditions and operating specifications.

Aside from the fundamentals, the principal compromise to the accuracy of extrapolations and interpolations is the interaction of the model parameters with the database parameters (e.g., tray efficiency and phase equilibria). Compromises in the model development due to the uncertainties in the data base will manifest themselves when the model is used to describe other operating conditions. A model with these interactions may describe the operating conditions upon which it is based but be of little value at operating conditions or equipment constraints different from the foundation. Therefore, it is good practice to test any model predictions against measurements at other operating conditions.

- The model that best describes the raw or adjusted measurements should be the model of choice.

The statistics literature presents numerous reviews of comparing the description of one model against another. Watanabe and Himmelblau (1984) present a list of review articles. The judgment criterion is based on a comparison of the model predictions against the measurements. These comparisons are related to the general statistic given below, developed for each model with its corresponding parameter set.

$$S^2 = \delta\vec{\mathbf{X}}_1^{M\mathrm{T}}\delta\vec{\mathbf{X}}_1^{M}$$

where

$$\delta\vec{\mathbf{X}}_1^{M} = \hat{\vec{\mathbf{X}}}_1^{M} - \hat{\vec{\mathbf{X}}}_1^{m}$$

Appropriate weighting and focus on a subset of measurements can be introduced as statistical knowledge of the measurements, end-use focus, and engineering judgment warrant. When weighted with the uncertainties in the adjusted measurements, the statistic is χ^2. Two models can be compared using an F-statistic. With appropriate hypothesis testing, the best model can be chosen. These statistical comparisons are not a replacement for sound measurements and sound model fundamentals. They should be used as a guide only. The difficulties are:

- The statistical distributions of the measurements are unknown.
- The resultant distribution of the parameter estimates are also unknown.
- The weighting is usually arbitrary with only a subset of the measurements used.
- The statistical test provides no insight into the accuracy of the engineering fundamentals, equipment nonlinearities, or parameter interactions.

Unfortunately, models are rarely exact. The semblance of sophistication inherent in the model and used to develop parameter estimates frequently masks their deficiencies. Models are only approximate, and their predictions when the parameter estimates are based on analysis of plant performance must be considered as approximate. Validation of the model and the parameter estimates using other operating conditions will reduce the likelihood that the conclusions have significant error.